## SYNTHESIS AND CHARACTERIZATION OF FULLERENE DOPED POLYANILINE/TITANIUM DIOXIDE NANOCOMPOSITES FOR ELECTROMAGNETIC INTERFERENCE SHIELDING

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FACULTY OF SCIENCE UNIVERSITY OF MALAYA KUALA LUMPUR

2018

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## DISSERTATION SUBMITTED IN FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE (EXCEPT MATHEMATICS & SCIENCE PHILOSOPHY)

## DEPARTMENT OF CHEMISTRY FACULTY OF SCIENCE UNIVERSITY OF MALAYA KUALA LUMPUR

2018

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# SYNTHESIS AND CHARACTERIZATION OF FULLERENE DOPED POLYANILINE/TITANIUM DIOXIDE NANOCOMPOSITES FOR ELECTROMAGNETIC INTERFERENCE SHIELDING ABSTRACT

Fullerene doped Polyaniline (PAni) nanocomposites were synthesized through template-free method at 0°C by using aniline (Ani) as monomer, fullerene and titanium dioxide (TiO<sub>2</sub>) as fillers. Fullerene doped PAni nanocomposites with chemical treatment by sulfonic groups such as dioctyl sodium sulfosuccinate (AOT), sodium dodecylbenzene sulfonicate (DBSA) and camphorsulfonic acid (CSA) were prepared to improve the dispersion of C<sub>60</sub> during polymerization. Besides, PAni nanocomposites with different types of fullerene ( $C_{60}$  and small gap fullerene (S.G.F)) and PAni nanocomposites with different contents of C<sub>60</sub>: (5 %, 10 %, 15 %, 20 % and 40 %) were synthesized. Fourier Transform Infrared (FTIR) and Ultraviolet-visible (UV-vis) spectra validated the functional groups and conducting behavior of fullerene doped PAni nanocomposites, respectively. The existence of fillers in PAni nanocomposites were confirmed by the characteristic peaks of TiO<sub>2</sub> and fullerene (C<sub>60</sub> and S.G.F) in X-ray diffraction (XRD) pattern. The morphology behaviors and electrical conductivity of fullerene doped PAni nanocomposites were investigated by Field Emission Scanning Electron Microscope (FESEM) and resistivity meter, respectively. Fullerene doped PAni nanocomposites with chemical treatment significantly improved the formation of nanorods/nanotubes which eventually increase the electrical conductivity  $(5.433 \times 10^{-2})$  $-1.708 \times 10^{-1}$  S/cm) as compared to those without chemical treatment (3.655  $\times 10^{-2}$ S/cm). Among all the PAni with chemical treatment, fullerene doped PAni that treated with CSA shows the highest amount of nanorods/nanotubes and electrical conductivity of  $1.708 \times 10^{-1}$  S/cm. Beside, PAni with addition of C<sub>60</sub> plays a good synergy effect which significantly enhance the electrical conductivity of PAni nanocomposites as

compared to PAni with addition of S.G.F. The electromagnetic interference (EMI) shielding properties of fullerene doped PAni nanocomposites were carried out by Microwave Vector Network Analyzer (MVNA) from frequency range of 0.5 GHz to 18.0 GHz. Based on the result, PAni nanocomposites with 40 % of C<sub>60</sub> that was treated with CSA possesses the poorest EMI shielding properties with a broad and weak reflection loss (RL) peak of -6.3 dB. This is because the lowest electrical conductivity, dielectric permittivity and heterogeneity of PAni nanocomposites will possess the weakest molecular polarization that leads to the poorest EMI shielding. However, PAni formulated with 10 % of C<sub>60</sub> that was treated with CSA revealed a narrow and sharp RL peak with the highest absorption (-61.3 dB) at 9 GHz. It is because the highest electrical conductivity (1.708 × 10<sup>-1</sup> S/cm), dielectric permittivity and heterogeneity (larger amount of nanorods/nanotubes) of PAni will induce more disordered motion of charge carrier along the PAni backbone, thus enhanced EMI shielding properties.

Keywords: Polyaniline, fullerene, electromagnetic interference shielding, reflection loss

# SINTESIS DAN PENCIRIAN NANOKOMPOSIT FULERENA DOP POLYANILINA/TITANIUM DIOKSIDA UNTUK PERISAI GANGGUAN ELEKTROMAGNETIK

### ABSTRAK

Nanokomposit fulerena dop polyanilina (PAni) telah disentesis melalui kaedah tanpa template pada suhu 0 °C dengan menggunakan aniline (Ani) sebagai monomer, fulerena dan titanium dioksida (TiO<sub>2</sub>) sebagai bahan pengisi. Nanokomposit fulerena dop polyanilina dengan rawatan kimia menggunakan pelbagai kumpulan sulfonik iaitu dioktil natrium sulfosuksinat (AOT), natrium dodesilbenzena sulfonikat (DBSA) dan asid kamforsulfonik (CSA) telah disediakan untuk membantu penyebaran C<sub>60</sub> semasa pempolimeran. Selain itu, nanokomposit PAni dengan pelbagai jenis fulerena (fulerena (C<sub>60</sub>) dan jurang kecil fulerena (S.G.F)) dan nanokomposit PAni dengan pelbagai kandungan C<sub>60</sub>: (5 %, 10 %, 15 %, 20 % dan 40 %) telah disentesiskan. Spektra Inframerah Transformasi Fourier (FTIR) dan Ultraungu-nampak (UV-vis) masingmasing telah mengesahkan kumpulan berfungsi dan ciri-ciri konduksi elektrik bagi nanokomposit fulerena dop PAni. Kewujudan bahan pengisi dalam nanokomposit PAni telah dibuktikan dengan kehadiran ciri puncak TiO<sub>2</sub> dan fulerena (C<sub>60</sub> dan S.G.F) dalam corak spektrum pembelauan sinar-X (XRD). Sifat morfologi dan kekonduksian elektrik bagi nanokomposit fulerena dop PAni telah dikaji masing-masing dengan menggunakan mikroskop pengimbas elektron (FESEM) dan meter perintang. Nanokomposit fulerena telah mempertingkatkan dop PAni dengan rawatan kimia pembentukan nanorod/nanotub dan menyebabkan peningkatan dalam kekonduksian elektrik (5.433  $\times$  $10^{-2}$  -  $1.708 \times 10^{-1}$  S/cm) jika dibangdingkan dengan sampel tanpa rawatan kimia  $(3.655 \times 10^{-2} \text{ S/cm})$ . Diantara kesemua PAni dengan rawatan kimia, fulerena dop PAni yang dirawat dengan CSA telah menunjukkan jumlah nanorod/nanotub yang paling tinggi dan kekonduksian elektrik tertinggi iaitu  $1.708 \times 10^{-1}$  S/cm. Selain itu, PAni

dengan penambahan C<sub>60</sub> memainkan kesan sinergi yang bagus dimana ia telah meningkatkan kekonduksian elektrik nanokomposit PAni jika dibandingkan PAni dengan penambahan S.G.F. Sifat perisai gangguan elektromagnetik (EMI) bagi nanokomposit fulerena dop PAni telah dijalankan dengan menggunakan pengesan rangkaian vektor mikro gelombang (MVNA) dalam julat frekuensi 0.5 GHz kepada 18.0 GHz. Berdasarkan keputusan yang diperolehi, nanokomposit dengan 40 % C<sub>60</sub> yang dirawat dengan CSA menunjukkan sifat perisai EMI yang sangat lemah dengan pembentukkan puncak (RL) yang luas dan penyerapan yang lemah iaitu -6.3 dB. Hal ini adalah disebabkan oleh kekonduksian elektrik, ketelusan dielektrik dan heterogeniti vang rendah bagi PAni yang mempunyai polarasi molekul yang lemah, akan membawa kepada sifat perisai EMI yang sangat lemah. Walau bagaimanapun, PAni diformulasikan dengan 10 % C<sub>60</sub> yang dirawat dengan CSA telah mendedahkan pembentukkan puncak kehilangan pantulan yang sempit dan tajam dengan nilai penyerapan yang tertinggi (-61.3 dB) pada 9.0 GHz. Ini disebabkan oleh kekonduksian elektrik (1.708  $\times$  10<sup>-1</sup> S/cm), ketelusan dielektrik, heterogeniti (jumlah nanorod/nanotub yang banyak) yang tertinggi bagi PAni akan mendorong pergerakan pembawa cas secara rawak disepanjang tulang belakang PAni, seterusnya meningkatkan sifat perisai EMI.

**Kata kunci:** Polyanilina, fulerena, sifat perisai gangguan elektrok magnetik, pembentukkan puncak

#### ACKNOWLEDGEMENTS

First of all, I would like to thank everyone who made this thesis is possible and enjoyable experience for me. Besides, I wish to express my sincere gratitude to my supervisor, Dr. Phang Sook Wai and Dr. Desmond Ang Teck Chye for their invaluable guidance, encouraging advices and consistent supervision to guide me in order to complete my research work. Their wide knowledge, valuable advice and encouragement have been of great value for me and will be remembered lifelong. It is a pleasure to have the oppurtinity to learn with them. Besides that, I would like to extend my warmest thanks to those whom have helped throughout my work especially to the staffs of Department of Chemistry for their kindness to help on my research work and Faculty of Science in completion of this research. In addition, special appreaciation expressed to Physic garage, Department of Physic for the preparation of pellet and toroid mould. I would also like to acknowledge to Mr. Masato Tadokoro from The Yokohama Rubber Co., Ltd, Japan for the assistance in the microwave absorption measurements. Last but not least, I would also like to express my deepest gratitude for a moral support, encouragement and understanding that I received from my family especially my parents (Rogayah Binti S. Abdullah and Mokhtar Bin Ibrahim), my husband (Aized Ilyas Bin Idris) and my daughter (Nurul Kawthar Bin Aized Ilyas). Finally, I would like to take this oppurtinity to thank all those whom I have not mentioned. Their direct and indirect assistance have had an impact to this project. The whole experience of pursuing this degree of master in science has taught me to be more independent, patient and understanding the true meaning of research.

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## LIST OF SYMBOLS AND ABBREVIATIONS

D	:	Diameter
dB	:	Decibels
I	:	Intensity of light
I。	:	Initial intensity of light
mm	:	Millimeter
<b>S</b> 11 <sup>*</sup>	:	Complex scattering parameters
S/cm	:	Conductivity unit in siemens per centimeter
Т	:	Transmission
Tan <b>ð</b>	:	Loss tangent
V	:	Voltage
Er'	:	Real part of dielectric permittivity
&r"	:	Imaginary part of dielectric permittivity
μr'	:	Real part of magnetic permeability
μr″	:	Imaginary part of magnetic permeability
π	:	Pi
°C	:	Degree celcius
σ	:	Conductivity
% T	:	% Transmission
Abs	:	Absorbance
Ani	:	Aniline
ΑΟΤ	:	Dioctyl sodium sulfosuccinate
APS	:	Ammonium persulphate
CNT	:	Carbon nanotubes

СР	:	Conducting polymer
CSA	:	Camphorsulfonic acid
C60	:	Fullerene
DBSA	:	Dodecylbenzene sulfonic acid
DSCC	:	Dye sensitized solar cell
EB	:	Emeraldine base
EM	:	Electromagnetic
EMA	:	Ethylene methyl acrylated
EMI	:	Electromagnetic interference
ES	:	Emeraldine salt
FESEM	:	Field Emission Scanning Electron Microscope
Fe <sub>3</sub> O <sub>4</sub>	:	Iron oxide
FTIR	:	Fourier Transform Infra-red
GHz	:	Gigahertz
НА	:	Hexanoic acid
номо	:	Highest occupied molecular orbital
LE	:	Leucoemeraldine
LED	÷	Light emitting diodes
LUMO	÷	Lowest unoccupied molecular orbital
MVNA	:	Microwave vector network analyzer
MWNT	:	Multi walled carbon nanotubes
PA	:	Poly (acetylene)
PAni	:	Polyaniline
PE	:	Pernigraniline
PEDOT	:	Poly (3, 4-ethylenedioxythiophene)
PPS	:	Poly (phenylene sulfide)

- **PPV** : Poly (para-phenyelene-vinylene)
- **PPy** : Polypyrrole
- PTh : Polythiophene
- **PVA** : Polyvinyl alcohol
- SEM : Scanning electron microscope
- S.G.F : Small gap fullerene
- SrTiO<sub>3</sub> : Strontium titanate
- **SWNT** : Single wall carbon nanotube
- TiO<sub>2</sub> : Titanium dioxide
- UV-Vis : Ultraviolet-visible
- **XRD** : X-ray diffractometer

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#### **CHAPTER 1: INTRODUCTION**

#### 1.1 Conducting Polymer (CP)

Polymers comprised of very large molecules that made up of many monomers that are covalently bonded together in long repetitive manner (Painter et al., 1977). Most of the common polymers are known to be a good electric insulator as the bonds present in common polymers are predominantly covalent and there is no free delocalized electron cloud in the system (Singh & MacRitchie, 2001).

Since the discovery of intrinsically conducting polyacetylene (PA) in 1970s by Alan Heeger, Alan MacDiarmid and Hideki Shirakawa, CP has attracted great interest and has significantly changed the cognizance that polymer cannot conduct electricity. They observed that when PA was exposed to halogen, the conductivity increased up to 10<sup>5</sup> S/cm which was considerably higher than any other traditional insulating polymer (Stejskal et al., 2017). With the invention and development of conductive PA, PC has received significant attention and the researchers who worked on it, Heeger and companion has won a Nobel Prize for the discovery of novel CP in year 2000 (MacDiarmid, 2001). Figure 1.1 shows a few examples of CP such as PA, Polypyrrole (PPy), Polypara-phenylene-vinylene, Poly (3, 4-ethylenedioxythiophene) (PEDOT) and PAni (Rikukawa & Sanui, 2000).



n and x = Number of repeating units

Figure 1.1 Chemical structures for various types of CP

Principally, CP can be classified as organic polymers that have the ability to conduct electricity. The most salient properties of CP that allows it to be conductive is the presence of conjugated  $\pi$ -bond system that has single and double bond alternating along the backbone of polymer chain. This organic CP can be oxidixed can reduced easily in the presence of charge transfer agents and through doping thet can achieve near metallic conductivity. The unique properties of CP have led to high demand for the polymer in various applications such as EMI shielding, dye sensitized solar cells (DSCC), light emitting diodes (LED), chemical sensor and biosensors (Wang & Jing, 2005; Geoffrey et al., 2003; Burroughes et al., 1990; Janata & Josowicz, 2003; Gerard et al., 2002).

## 1.2 Polyaniline

Among all CP, PAni is the most extensively studied due to its unique electrical, chemical and physical behaviors. PAni exhibits different colors corresponding to its redox state, which are yellow for leucoemeraldine (LE), blue for emeraldine base (EB), green for emeraldine salt (ES) and purple for pernigraniline (PE). In principal, the terms LE, EB and PE refer to different oxidation state of PAni where n = 1 for the completely reduced, n = 0.5 for the half oxidized and n = 0 for the fully oxidized of PAni, respectively as shown in Figure 1.2 (Chiang & MacDiamid, 1986).

In addition to that, PAni can be converted from one oxidation state to another oxidation state through doping and dedoping process reversibly with apparent color changes. This property is unique to PAni, and not observed in other CP (Figure 1.2) (Kim et al., 2009). Due to the unique properties of PAni such as highly conductive, excellent EMI shielding properties, lightweight, corrosion resistivity, ease of synthesis and high durability, it can be potentially applied as EMI shielding material (Belaabed et al., 2012; Pandey & Ramontja, 2016; Lapinsky & Easty, 2006; Geetha et al., 2009).



Figure 1.2: The reversible reaction of PAni in different oxidation state

(Adopted from: Chiang, J. C. & MacDiarmid, A. G. (1986). 'Polyaniline': Protonic Acid Doping of Emeraldine Form to The Metallic Regime. Synthetic Metals, 13 (1-3), 193-205.

## **1.3** Electromagnetic interference (EMI) shielding properties

In practice, the EM waves in the radio frequency spectrum that passes through the air will interrupt the operation of electronic devices and significantly led to EMI noises. In order to minimize the EMI problem, EMI shielding materials need to be developed.

Generally, electrical conductivity, dielectric permittivity and magnetic permeability are the main factors that play an important role in order to design a good performance of EMI shielding material (Xia et al., 2016). Recently, many researchers study the combination of PAni that possesses a high electrical conductivity with dielectric material (titanium dioxide, TiO<sub>2</sub>) that significantly will increase the electrical conductivity and dielectric permittivity more than the individual components (Mo et al., 2008; Marija et al., 2010).

Basically, TiO<sub>2</sub> known as dielectric materials that possess dielectric constant in range of 60 - 80 (Wypych et al., 2014). On the other hand, the dielectric constant of PAni is 20 -30 (Khalil, 2014). The combination of TiO<sub>2</sub> and PAni suddenly increased the dielectric constant up to 150 - 200 due to the synergetic effect between PAni and TiO<sub>2</sub> (Mo et al., 2008). Thus, TiO<sub>2</sub> is a good candidate to combine with PAni in order to produce PAni with high dielectric constant for better EMI shielding.

Besides that, the introduction of carbonaceous material such as carbon nanotubes (CNT), graphene and multi-wall carbon nanotubes (MWNT) into PAni also attract great interest in EMI shielding. It is because the carbonaceous material not only can increase the conductivity of the PAni nanocomposites but also improve the surface area for EMI shielding (Bhadra et al., 2009: Qin & Brosseau, 2012).

Recently, much attention also has been focused (carbonaceous material), which is one of the new allotropic forms of pure carbon that possesses interesting chemical and physical properties that can be applied as semiconductor materials. Principally, fullerene is known as carbonaceous materials with a non-conductive behavior (Bronnikov et al., 2017). Pristine PAni possess low conductivity of  $10^{-6} - 10^{-9}$  S/cm based on previous research study (Thanh-Hai et al., 2017). However, addition of fullerene into PAni signicantly increased up the conductivity to  $10^{-4} - 10^{-3}$  S/cm (Xiong et al., 2012). This is because the synergistic effect between PAni as electron donors and fullerene as electron acceptors will produce more mobile electron and mobile cation, thus increase the electrical conductivity of PAni/fullerene. Based on our knowledge, the combination of PAni with TiO<sub>2</sub> (dielectric material) and fullerene (carbonaceous material) in EMI shielding application is still new and the firstly reported here.

#### **1.4 Problem statement**

In this modern time, the proliferation of electronic devices, medical equipment and stealth technology of aircraft has led to an EMI noise or pollution, which is also known as EMI. The noise or pollution from electronic devices may cause the malfunction of instruments (Geetha et al., 2009; Lapinsky & Easty, 2006). Therefore, EMI shielding material is extremely important to protect the electronic devices by eliminating unwanted EM radiation (Kim et al., 2002).

Metal is the most common EMI shielding material (Figure 1.3) due to its good reflection properties. However, metal primarily reflects the radiation but is unable to absorb the EM wave due to its shallow skin depth, thus limited its application (Singh & Kulkarni, 2014). Besides, metal has several drawbacks such as high density, heavy, vulnerable to corrosion and uneconomical processing. Compared with traditional EMI shielding material such as metal, CP has inspired much interest in EMI shielding application recently due to its unique properties such as lightweight, corrosion resistivity, high metallic conductivity and wide absorbing range (Chung, 2000; Jing, Wang & Zhang, 2005; Joo & Epstein, 1994).

Generally, conductivity, dielectric permittivity and magnetic permeability are the main factors that lead to a good EMI shielding properties. In this study, the combination of PAni, TiO<sub>2</sub> and fullerene is proposed to enhance the conductivity, dielectric permittivity and magnetic permeability of PAni nanocomposites that may contribute to excellent EMI shielding. This novel combination is still new and reserved a space to be explored.



Figure 1.3 Example of conventional EMI shielding material

In this research study, fullerene doped PAni nanocomposites, which comprised of Ani as monomer,  $TiO_2$  as dielectric material and fullerenes ( $C_{60}$  and S.G.F: small gap fullerene) as carbonaceous material will be synthesized through template-free method. The EMI shielding properties of fullerene doped PAni nanocomposites will be investigated using Microwave Vector Network Analyzer (MVNA) from 0.5 GHz to 18.0 GHz. Besides, the effect of EMI shielding properties of fullerene doped PAni anacomposites will be studied by different types of fullerene ( $C_{60}$  and S.G.F) without and with chemical treatment using different types of sulfonic groups.

#### **1.5** Research objectives

The research objectives in this study are listed below:

(i) To synthesize fullerene doped PAni nanocomposites using different synthesis parameters (chemical treatment with different types of sulfonic groups, doped with different types and contents of fullerene) through template-free method.

- (ii) To characterize the fullerene doped PAni nanocomposites by using Fourier Transform Infrared (FTIR) spectrometer, Ultraviolet-Visible (UV-Vis) spectrometer, X-ray diffractometer (XRD), Field Emission Scanning Electron Microscope (FESEM) and resistivity meter.
- (iii) To measure the EMI shielding properties of fullerene doped PAni nanocomposites by Microwave Vector Network Analyzer (MVNA).

#### **CHAPTER 2: LITERATURE REVIEW**

### 2.1 Conducting polymer (CP)

The higher electrical conductivity of CP has led to the name of 'synthetic metal' (MacDiarmid, 2001). Sometimes, conjugation itself is inadequate for the CP to be highly conductive to be applied in various applications such as dye-sensitized solar cell, chemical sensor, photodegradation and so on. Introduction of dopant in polymer chain is crucial as it creates and allows the charge carrier in electric field and consequently increased the electrical conductivities of the polymer. Doping can be done either by removal (p-doping) or addition (n-doping) of electron from the polymer chain, which is commonly known as oxidation and reduction, respectively (Freund & Lewis, 1995).

This configuration will create extra holes (positive charges) or electrons (negative charge) that can reduce the band gap energy between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), and consequently increase the mobility of charge carriers along the polymer backbone, thus increase the electrical conductivities.

Since the discovery of the first conductive PA by Alan Heeger, Alan MacDiarmid and Hideki Shirakawa in year 1970, others CP such as PPy, PTh, PEDOT and etc also have been discovered in the following years by others researchers. According to Sujata and co-workers, PPy thin film were synthesized by a simple and cost-effective chemical bath deposition method. The electrochemical supercapacitive properties of Ppy thin films were measured by cyclic voltammety. Based on the data obtained, PPy thin films exhibited the highest capacitance of 329 Fg<sup>-1</sup> at the scan rate of 5mVs<sup>-1</sup> that eventually makes Ppy as a promising electrode for supercapacitors (Sujata et al., 2013). Besides, PTh also can be potentially applied in sensor application. In year 2014, PTh nanotubes was prepared through electrochemical polymerization by Ali and co-workers, and was successfuly employed as a new electrochemical sensor in riboflavin detection. This PTh sensor was able to detect riboflavin from 0.01 to 65  $\mu$ M with a low detection limit of 3  $\mu$ M. This sensor also possessed an accurate and rapid response to riboflavin with good sensitivity, stability and repeatability (Ali et al., 2014).

In the same year, Samba and co-workers were studied the application of PEDOT with CNT as electrochemical sensing material for neurotransmitters in catecholamines. The PEDOT-CNT microelectrodes is able to detect as low as 1  $\mu$ M concentration of dophamine in the presence of uric acid and ascorbic acid. Besides, other types of catecholamines such as serotonin, epinephrine, norepinephrine and L-dopa are also electrochemically detecable by PEDOT-CNT microelectrodes (Samba et al., 2014).

Aphesteguy and co-worker have carried out the research by using PAni-ES that possess high conductivity, excellent dielectric permeability and magnetic permeability for microwave absorption study (Aphesteguy et al., 2012). PAni-ES also was implemented in solar cell technologies due to its high electro catalytic activity (Xiao et al., 2014). Furthermore, the most popular application of PAni-ES is optical and chemical sensor due to its excellent sensing properties such as good flexibility, excellent environmental stability and ability to make physical and chemical interaction during exposure to chemical solutions (Nguyen et al., 2015; Xue et al., 2017).

Kavirajaa and co-workers has designed a simple chemical sensor for hydrazine detection using PAni-ES thin film. The PAni-ES was synthesized through chemical oxidation method in the present of sodium bis (2-ethyl hexyl) sulfosuccinate (AOT) dopant. The presence of 2-ethylhexyl groups on AOT would reduce the interaction between PAni chains and increase its affinity and solubility in non-polar organic solvent. In addition to that, the presence of oxygen atom on ester and sulfonate group on AOT would increase solubility of PAni in polar organic solvent. In their study, PAni with highest concentration of AOT possessed high conductivity (0.4-0.8 S/cm), good sensitivity with fast responds time (7 seconds) and good reusability up to 10 cycles during hydrazine detection. Thus, addition of AOT dopant not only improves the solubility but also enhance the conductivity and processability of PAni thin film as a chemical sensor in hydrazine detection (Kavirajaa et al., 2015).

#### 2.2 Polyaniline (PAni)

Principally, PAni can convert from one oxidation state to another oxidation state easily and reversible which others CP do not possess this ability (MacDiarmid et al., 1987). Among all oxidation states of PAni, PAni is ES form is commonly applied as promising materials in various applications due to its excellent conductive and electrochemically active properties compared with others PAni form.

Due to the unique behaviors of PAni, PAni can potentially apply in numerous applications such as solar cells, sensor, photodegradation and so on. For example, PAni composites that doped with transition metal ions and MWNT that synthesized by Wu and co-workers were successfully applied as a counter electrode (CE) in dye-sensitized solar cells (DSCCs). The catalytic activity of MWNT-PAni that doped with Ni<sup>2+</sup> and Co<sup>2+</sup> as CE in DSCC revealed the power conversion efficiencies (PCE) of 6.00 % and 5.75 % which is much higher than the PCE of pristine MWCNT-PAni (4.58 %) (Wu et al., 2016).

Besides, PAni-coated titanium oxide (PTO) nanocomposites that was synthesized by Debnath and co-workers was successfully applied in catalytic photo-degradation of anionic dyes Eosin Yellow (EY) and Naphthol blue black (NBB). The initial dye concentration, pH and dosage are the factors that affected the photo-degradation process for EY and NBB. Based on the data obtained, pH of 3.0, initial dye concentration of 15 mg/L and catalyst dosage of 1.0 g/L exhibited the highest degradation of 99.85 % and 99.74 % for EY and NBB, respectively. Hence, it can be suggested that PTO is an efficient catalyst for the degradation of EY and EB (Debnath et al., 2015).

#### 2.3 EMI shielding material

Nowadays, there has been a growing and worldwide interest towards the development technology of EM wave in the higher gigahertz (GHz) ranges such as in the wireless communication system, radar, medical equipment and so on. However, EMI may interrupt the performance of these instruments that diminish their lifetime and affect the safety operation system of these electronic devices. Therefore, EMI shielding materials are developed in order to reduce the disastrous behavior of the EM noise and pollution (Dong-Hwan et al., 2016).

Metal and carbon black are the most common and traditional materials used to shield EMI due to its good mechanical and shielding properties. Recently, there are some studies reported by using metal as EMI shielding material. Poorbafrani and co-workers were studied the microwave absorption of cobalt-zinc-ferrite (Co<sub>0.6</sub>Zn<sub>0.4</sub>Fe<sub>2</sub>O<sub>4</sub>) nanoparticles. The high saturation magnetization (110 emu/g) and coercivity of Co<sub>0.6</sub>Zn<sub>0.4</sub>Fe<sub>2</sub>O<sub>4</sub> significantly enhanced the utilizing stoichiometry, coordinate agent and sintering temperature. With these factors, it has found that Co<sub>0.6</sub>Zn<sub>0.4</sub>Fe<sub>2</sub>O<sub>4</sub>-paraffin that containing 20 wt % of paraffin, revealed the highest microwave absorption properties with RL of -23.6 dB at 7.0 GHz as compared to the traditional spinel ferrite. (Poorbafrani & Kiani, 2016).

The flexible and thin layer microwave absorber based on carbon black-nitrile rubber composites (CBSrF) have been fabricated by Vinayasree and co-workers, and their RL properties were studied in the S (2-4 GHz) and X bands (8-12 GHz). In this study, the

content of CBSrF can be modified in order to tune the microwave absorption of the composite. Based on the data obtained, 50 % of CBSrF exhibited the best microwave absorption with RL of -28 dB at 2.55 GHz (S band) and for the X band, the highest RL is -16 dB at 11.2 GHz. The incorporation of CB into composites significantly enhanced the microwave absorption properties and wider the bandwidths as compare to the pure SrF composites. (Vinayasree et al., 2014).

However, the application of traditional materials (metal and carbon black) possess several drawbacks like high density, costly processing, vulnerable to corrode and uneconomic processing (Oghbaei & Mirzaee, 2010). Besides, metal primarily reflects radiation but it is unable to absorb the EM wave due to its shallow skin depth that limits its application in EMI shielding (Petrov & Gagulin, 2001).

#### 2.4 Application of PAni nanocomposites as EMI shielding material

In order to overcome the drawbacks of traditional material, CP especially PAni has been appointed as promising EMI shielding materials due to its unique properties such as facile synthesis, low density, present in different colors corresponding to their redox state, possess high conductivity  $(10^{-5} - 10^{-3} \text{ S/cm})$  and able to absorb and reflect the EM radiation (Thomassin et al., 2010; Yuping et al., 2006).

Principally, EMI shielding materials consists of mobile charge carriers or electric and magnetic dipoles that will interact with EM fields in the radiation (Colaneri & Schacklette, 1992). Figure 2.1 shows the interaction between EM waves and shielding material during EMI shielding application. Based on the Figure 2.1, S<sub>1</sub> is referring to wave at plane 1, while S<sub>2</sub> is refer to wave at plane 2. The complex scattering (S) parameters for S<sub>11</sub> (or S<sub>22</sub>) and S<sub>12</sub> (or S<sub>21</sub>) are refer to the reflection and transmission of EM waves, respectively for microwave vector network analyzer (MVNA) system. The difference between S<sub>11</sub> and S<sub>22</sub> is the reflection is come from wave plane at plane 1 and 2, respectively. During the EMI shielding application, the target is to reduce the transmission ( $S_{12}$  or  $S_{21}$ ) to zero as well as to maximize the reflection ( $S_{11}$  or  $S_{22}$ ) or increase the absorption of EM waves in order to perform excellent EMI shielding properties (Zhang et al., 2017).



Figure 2.1: EMI shielding application: Interaction between EM waves with shielding material

(Adopted from: Zhang, Y., Wang, Z., Zhang, B., Zhao, G. L., & Guo, S. M. (2015). The Electromagnetic Interference Shielding Effectiveness of High Aspect-Ratio SiC Nanofibers/Exposy Composites. Royal Society of Chemistry, 5, 93499-93506).

A compound having high conductivity, dielectric permittivity and magnetic permeability would potentially be able to exhibit excellent EMI shielding characteristics (Maity et al., 2013). In order to improve the dielectric permittivity and magnetic permeability for the EMI shielding properties, many researchers study about the combination of PAni with dielectric material (TiO<sub>2</sub>) and carbonaceous materials such as carbon nanotubes (CNT), single wall carbon nanotubes (SWNT), multi wall carbon nanotubes (MWNT), graphene and so on.

In the few decades, TiO<sub>2</sub> as dielectric materials has paid more attention due to its special surface, electronic and photocatalytic behavior. Hence, TiO<sub>2</sub> doped PAni has reveal a promising dielectric and mechanical property in EMI shielding application. Mo and co-workers have studied the dielectric properties of PAni with TiO<sub>2</sub> nanoparticles and TiO<sub>2</sub> colloidal. Based on the morphology studies, PAni with TiO<sub>2</sub> nanoparticles revealed a uniform distribution as compared to PAni with TiO<sub>2</sub> colloids. The uniform distribution of PAni significantly increase the dielectric constant and dielectric loss due to the better charge transfer in the PAni network (Mo et al., 2008).

At the same time, Phang and co-workers have prepared hexanoic acid (HA) doped PAni that containing TiO<sub>2</sub> nanoparticles (PAni/HA/TiO<sub>2</sub>) with different synthesis temperature (0 °C and 25 °C). Based on morphology study, PAni/HA/TiO<sub>2</sub> synthesized at 0 °C induced more formation of nanorods/nanotubes with the larger diameter as compared with those synthesized at 25 °C. Among all PAni nanocomposites, PAni/HA/TiO<sub>2</sub> that synthesized at 0 °C exhibited the highest permittivity and heterogeneity that lead to a good microwave absorption property (>99.0 % absorption) with RL of -31 dB at 10 GHz (Phang et al., 2008).

Moreover, Xu and co-workers have investigated the conductivity of PAni with different contents of TiO<sub>2</sub>. Based on the result obtained, the addition of TiO<sub>2</sub> from 0 % to 5 % (optimum level) of doped PAni significantly increased the conductivity from 1.6  $\times$  10<sup>-2</sup> S/cm (pristine PAni) to 7.4  $\times$  10<sup>-1</sup> S/cm, respectively. This may be attributed to the doping effect associated with TiO<sub>2</sub> nanoparticles that induce the formation of more efficient network for the charge transfer, thus enhancing the conductivity of the doped PAni. However, the increasing of TiO<sub>2</sub> after the optimum level, the electrical conductivity of doped PAni significantly decreased due to the blockage of the

conductive pathways by larger amount of TiO<sub>2</sub> that embedded in PAni matrix (Xu et al., 2005).

According to Deng and co-workers, PAni-Fe<sub>3</sub>O<sub>4</sub> nanoparticles with core-shell structure were synthesized by in situ emulsion polymerization. PAni-Fe<sub>3</sub>O<sub>4</sub> nanoparticles showed ferromagnetic behavior with high-saturated magnetization ( $M_s = 4.2 - 48.4 \text{ emu/g}$ ) and high coercive force ( $H_c = 8.1 - 55.3 \text{ Oe}$ ). However, the conductivity of PAni-Fe<sub>3</sub>O<sub>4</sub> was significantly decreased to  $1.53 \times 10^{-3}$  S/cm due to the insulating behavior of the Fe<sub>3</sub>O<sub>4</sub>. Besides, it was found that the increasing of Fe<sub>3</sub>O<sub>4</sub> content will significantly affect the doping degree of PAni, thus reduced the electrical conductivity of the PAni-Fe<sub>3</sub>O<sub>4</sub> (Deng et al., 2003).

According to Ting and co-workers, PAni/MWNT has been synthesized by in situ polymerization. Based on the morphology study, the diameter of PAni/MWNT was larger than pure MWNT due to the uniform coating of PAni on MWNT layer during polymerization. PAni/MWNT possessed the highest dielectric permittivity (1.7) and magnetic permeability (1.0), which are the main factors that lead to the best microwave absorption with RL of -14.1 dB at 11.5 GHz (Ting et al., 2012).

Recently, many researchers have been focused on the combination of PAni with dielectric and carbonaceous materials (DWNT, MWNT, CNT and so on) in order to improve the EMI shielding properties. According to Koh and co-workers, PAni/HA/TiO<sub>2</sub>/DWNT with and without chemical treatment has been successfully prepared by template-free method. In this study, PAni nanocomposites with treated DWNT induced the formation of more nanorods/nanotubes. This phenomena significantly created more space charge polarization along the PAni chain, thus significantly enhanced the conductivity pathway of PAni. Besides, the higher magnetic permeability of PAni nanocomposites with treated DWNT will induce the eddy current
of PAni. Due to the highest conductivity, dielectric permittivity and magnetic permeability of PAni nanocomposites with treated DWNT, the microwave absorption significantly improve the RL of -18.3 dB as compared to those without chemical treatment (Koh et al., 2016).

According to Phang and co-workers, it was found that the addition of  $TiO_2$  and carbonaceous materials (SWNT) would eventually enhance the magnetization, dielectric and conductivity of PAni and thus improve the microwave absorption of PAni. The resulted nanorods/nanotubes based on SEM images, it clearly shows that some CNT was enwrapped with PAni layer that indicated CNT just packed underneath PAni. The conductivity of PAni/HA/TiO<sub>2</sub>/SWNT shows a significant improvement after the addition of CNT because CNT formed a bridge that connect one PAni chain to another PAni chain in order to facilitate the movement of charge carriers among the intrachain of PAni. The magnetization of PAni/HA/TiO<sub>2</sub>/SWNT is significantly improved, thus created the magnetic influence such as increasing of anisotropy or eddy current that will induce the microwave absorbing of PAni. Based on result obtained, PAni/HA/TiO<sub>2</sub>/SWNT with 20 % of SWNT possessed the highest microwave absorption (~99.2 % absorption) with RL of -21.7 dB due to the high conductivity, magnetization, heterogeneity (large amount of nanorods/nanotubes) which might cause more disordered motion of charge carriers and exhibit greater molecular polarization (Phang et al., 2008).

Fullerene is one of the new allotropic forms of pure carbon compound (carbonaceous material) that has been discovered in 1985 by Richard Smalley, Robert Curl, James Heath and Harold Kroto (Georgakilas et al., 2015). Fullerene has been paid more attention in scientific society because it possesses fascinating chemical and physical properties (Kanwal et al., 2005). Figure 2.2 shows the several allotropic forms

of fullerenes. Fullerene is as outstanding electron acceptor, for instance, fullerenes become superconductor at low temperature when doped with alkali metals (Da Ros et al., 2001).



**Figure 2.2:** Different allotropic forms of fullerenes: (a)  $C_{60}$ , (b) S.G.F, (c)  $C_{70}$  and (d)  $C_{540}$ 

(Adopted from: Lim, H. Y., Jeong, S. K., Suh, J. S., Oh, E. J., Park, Y. W., Ryu, K. S., & Yo, C. H. (1995). Preparation and Properties of Fullerene Doped Polyaniline. Synthetic Metals, 70 (1-3), 1463-1464).

Previously, studies of  $C_{60}$  with PAni composites were mainly centered on the nature of the interaction between PAni and  $C_{60}$  in the composites materials. The synergy effect between PAni as electron donors and  $C_{60}$  as electron acceptors has made them as p-type semiconductor as reported by Lim and co-workers. Based on the cyclic voltammogram, the redox process of PAni/ $C_{60}$  was shifted to higher potential of redox reaction. This may be attributed to the steric effect of bulky  $C_{60}$  and electronic effect caused by the electron withdrawing nature of  $C_{60}$ . Based on the result obtained, it significantly proved the formation of charge transfer between PAni (electron donor) and  $C_{60}$  (electron acceptor) (Lim et al., 1995).

In general, preparation of PAni with  $C_{60}$  is facing a dispersion problem due to the agglomeration of  $C_{60}$  during polymerization. Thus, the dispersion problem of  $C_{60}$  has been overcome by Dai and co-workers, which have reported the effect of chemical treatment (sulfonic groups) of  $C_{60}$  during the preparation of PAni/ $C_{60}$  composites. The sulfonated fullerene doped PAni (with chemical treatment) showed better dispersion in PAni with an enhancement of electrical conductivity of 100 S/cm as compared to those without chemical treatment (Dai et al., 1998).

Small gap fullerene (S.G.F) is one the fullerene that consists the mixture of fullerene from  $C_{60}$  to  $C_{84}$  and higher. Nevertheless, to the best of our knowledge, there are only few literature studies about the preparation of PAni and S.G.F. In year 2013, Politakos and co-workers have studied the conductivity systems in both PAni doped  $C_{60}$  and PAni doped S.G.F. The electrical conductivity of PAni doped S.G.F showed the lowest conductivity due to the larger size of S.G.F ( $C_{60}$  to  $C_{84}$  and higher) that distorts the intra chain transfer along the PAni chain. The steric hindrance caused by the bulky S.G.F will act as a barrier that blocked the conductive pathway along the PAni and thus reduced the electrical conductivity. In this study, it can be concluded that the conductivity of PAni are significantly affected by the type of fullerene, doping level and the way in which fullerene are incorporated into the polymer chains (Politakos et al., 2013).

Finally, based on the literature above, the research idea of this study had been modified based on the effect of EMI shielding properties of fullerene doped PAni nanocomposites using different types of fullerene ( $C_{60}$  and S.G.F) without and with

chemical treatment by using different types of sulfonic groups (such as AOT, DBSA and CSA) in order to improve both the dispersion (fullerene) and conductivity of PAni.

#### 2.5 Summary of literature review

In general, high electrical conductivity, dielectric permittivity and magnetic permeability are the main factors that contribute to excellent of EMI shielding properties of microwave absorption (Chung, 2000). Practically, the high electrical conductivity of material can be modified by using CP such as PPy, PTh, PEDOT and PAni (Gordana, 2013). In this study, PAni was chosen because PAni can easily change from one oxidation state to another oxidation state reversibly in which others CP does not.

The dielectric permittivity can be enhanced by the addition of dielectric material such as (TiO<sub>2</sub>, SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, Sm and so on) (Singh and Kulkarni, 2014; Mo et al., 2008). Finally, the introduction of carbonaceous materials (such as CNT, SWNT, DWNT, MWNT and so on) can enhance the magnetic permeability as well as the conductivity of the composites (Thomassin et al., 2013).

Table 2.1 shows the summary of literature review based on EMI shielding studies. Refer to Table 2.1, modification of conductivity and dielectric permittivity by using PAni/TiO<sub>2</sub> and Al/SiC were done by Phang and co-workers and Kuang and co-workers with RL range of –25 dB to -31 dB (Phang et al., 2008; Kheradmand et al., 2015). In year 2012-2017, enhancements of EMI shielding properties that modified by PAni and other magnetic materials such as (SWNT, DWNT, MWNT, Fe<sub>3</sub>O<sub>4</sub> and so on) revealed RL range of -14 dB to -49 dB (Ting et al., 2012; Liu et al., 2014; Liu et al., 2017; Feng et al., 2016; Nikmanesh et al., 2016; Qi et al., 2016). The improvement of conductivity, dielectric permittivity and magnetic permeability properties through addition of CP (PAni), dielectric materials (such as TiO<sub>2</sub>, Sm, SrTiO<sub>3</sub> and etc) and magnetic materials (such as Fe<sub>3</sub>O<sub>4</sub>, DWNT, SWNT, graphene and etc) by several researchers exhibited the RL range of -18 dB to -58 dB (Koh et al., 2013; Koh et al., 2016; Phang et al., 2008; Luo et al., 2014; Dorraji et al., 2016; Xu et al., 2015; Hosseini et al., 2015; Liu et al., 2013;Koh et al., 2017).

EMI shielding properties	<b>Research studies</b>	Author	RL (dB)	Year
Conductivity,	PAni/HA/TiO <sub>2</sub>	Phang et., al	-31	2008
dielectric permittivity	Al/SiC whiskers	Kheradmand et., al	-25	2015
	PAni/MWNT	Ting et., al	-14	2012
	PAni/Fe <sub>3</sub> O <sub>4</sub>	Liu et., al	-35	2014
Conductivity, magnetic permeability	Co <sub>0.2</sub> Ni <sub>0.4</sub> Zn <sub>0.4</sub> Fe <sub>2</sub> O <sub>4</sub> /graphene oxide	Liu et., al	-49	2017
	Coiled CNT/CoFe <sub>2</sub> O <sub>4</sub>	O <sub>4</sub> Feng et., al		2016
	MWNT/barium hexaferrite	Nikmanesh et., al	-23	2016
	Fe/helical CNT	Qi et., al	-47	2016
	PAni/TiO <sub>2</sub> /Fe <sub>3</sub> O <sub>4</sub>	Koh et., al	-49	2013
	PAni/TiO <sub>2</sub> /DWNT	Koh et., al	-18	2016
	PAni/TiO <sub>2</sub> /SWNT	Phang et., al	-22	2008
Conductivity,	PAni/Sm/SrFe <sub>11.7</sub> O <sub>19</sub>	Luo et., al	-24	2014
dielectric permittivity and magnetic	PAni/Fe <sub>3</sub> O <sub>4</sub> /ZnO polyester	Dorraji et., al	-10	2016
permeability	PAni/reduced graphene oxide/flake carbonyl iron	Xu et., al	-38	2015
	PAni/SrTiO <sub>3</sub> /SrFe <sub>12</sub> O <sub>19</sub>	Hossein et., al	-15	2015
	PAni/reduced graphene oxide/Co <sub>3</sub> O <sub>4</sub>	Liu et., al	-32	2013
	PAni/TiO <sub>2</sub> /MWNT	Koh et., al	-58	2017

**Table 2.1:** The summary of literature review based on EMI shielding studies

Based on our knowledge, at this juncture, the combination of PAni as conducting material, TiO<sub>2</sub> as dielectric material and fullerenes as carbonaceous material for EMI shielding application is still new and reserves a space to be explored. Thus, in this study, the EMI shielding properties of fullerene doped PAni with chemical treatment, different types of fullerenes and different content of fullerene is firstly reported here.

University Malaya

#### **CHAPTER 3: METHODOLOGY**

#### 3.1 Chemicals

The chemicals such as aniline (Ani) as monomer, hexanoic acid (HA) with purity of 99 % as dopant, ammonium persulphate (APS) as oxidant, titanium dioxide (TiO<sub>2</sub>) nanoparticles with particle size of < 30 nm, different types of fullerene (C<sub>60</sub> and small gap fullerene (S.G.F)), dioctyl sodium sulfosuccinate (AOT), sodium dodecylbenzene sulfonicate (DBSA) and camphorsulfonic acid (CSA) used in this study were purchased from Sigma-Aldrich. Methanol with purity of 99.8 % for washing purposes was supplied from Systerm. Distilled water used for polymerization was purified by simple distillation. All other reagents were used without further purification unless noted.

#### 3.2 Apparatus

The apparatus used during polymerization of fullerene doped PAni nanocomposites were beaker, measuring cylinder, droppers, spatula, dropping funnel and micropipette. On the other hand, agate mortar and pestle, petri dish, pellet mould, toroid mould and etc were used for the sample preparation of PAni nanocomposites for electrical conductivity measurement and microwave absorption studies.

#### **3.3** Experimental

## 3.3.1 Synthesis of PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> nanocomposites treated with different types of sulfonic groups

PAni nanocomposites containing  $TiO_2$  and  $C_{60}$  without chemical treatment was synthesized through template-free method using APS as an oxidant. Note that the amount of  $TiO_2$  and  $C_{60}$  are expressed as % relative to the amount of the Aniline monomer. Example, in formulation that uses 1.0 g of Aniline, 10 % of  $TiO_2$  is equivalent to 10 % of 1.0 g, i.e. 0.1 g. First, HA (1 mmol) was mixed with distilled water for 30 minutes followed by the addition of Ani (1 mmol). After that, 10 % of TiO<sub>2</sub> (0.10 g) and 10 % of C<sub>60</sub> (0.10 g) were added into the solution mixture and then stirred overnight in order to obtain a better dispersion of Ani/HA/TiO<sub>2</sub>/C<sub>60</sub> solutions. Subsequently, APS aqueous solution (1 mmol) was added dropwise to initiate the polymerization and continued under undisturbed condition at 0 °C. After 24 hours of polymerization, the synthesized PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> nanocomposites were then washed with distilled water followed by methanol three times, respectively. Finally, the nanocomposites were dried in oven at 60 °C for overnight.

For PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> nanocomposites with chemical treatment by sulfonic groups, C<sub>60</sub> was first added into 0.1 mmol of AOT aqueous solution and stirred for 30 minutes in order to disperse C<sub>60</sub> homogeneously before the polymerization start. After that, HA, Ani, and TiO<sub>2</sub> nanoparticles were added into the solution and stirred for overnight to get a homogenous solution. Then, APS was added dropwise and polymerization was continued overnight under undisturbed condition at 0 °C. The same polymerization method for PAni nanocomposites with chemical treatment was carried out by using different types of sulfonic group such as DBSA and CSA. The flow chart for synthesis of PAni nanocomposites was illustrated in Figure 3.1.



Figure 3.1: Flow chart of synthesis PAni nanocomposites

# 3.3.2 Synthesis of PAni nanocomposites without and with different types of fullerene

Among all PAni nanocomposites without and with chemical treatment, PAni nanocomposites that was treated with CSA shows a better EMI shielding property. Thus the synthesis of PAni nanocomposites treated by CSA was proceeding for without and with different types of fullerenes such as  $C_{60}$  and S.G.F. The  $C_{60}$  has a regular and spherical shape like buckminsterfullerene, while S.G.F has irregular shape (spherical and elongated) since S.G.F consists the mixture of fullerene from  $C_{60}$  to  $C_{84}$  and higher. The morphology of fullerene will significantly affect both the conductivity and EMI shielding of PAni nanocomposites. The same polymerization method in Part 3.3.1 (Paragraph 2) was repeated for PAni nanocomposites without and with different types of fullerene as shown in Table 3.1

PAni nanocomposites	Ani (mmol)	HA (mmol)	TiO2 (wt %)	Fullerenes (wt %)	CSA (mmol)
PAni/HA/TiO2		1	10	0	0.1
PAni/HA/TiO2/C60	1	1	10	10	0.1
PAni/HA/TiO <sub>2</sub> /S.G.F	1	1	10	10	0.1

Table 3.1 Synthesis of PAni without and with different types of fullerene

## 3.3.3 Synthesis of PAni nanocomposites with different contents of C<sub>60</sub>

Among all PAni nanocomposites without and with different types of fullerene,  $PAni/HA/TiO_2/C_{60}$  shows a better EMI shielding properties based on the result obtained. Therefore, the same polymerization methods as shown in Part 3.3.2 were

repeated for PAni nanocomposites with different contents of  $C_{60}$  (5 %, 10 %, 15 %, 20 % and 40 %) as shown in Table 3.2.

PAni nanocomposites	Ani mmol	TiO2 wt %	C60 wt%
	(g)	(g)	(g)
PAni/HA/TiO2/C60 (5 %)	1.00	10	5
	(0.90)	(0.10)	(0.05)
PAni/HA/TiO2/C60 (10 %)	1.00	10	10
	(0.90)	(0.10)	(0.10)
PAni/HA/TiO2/C60 (15 %)	1.00	10	15
	(0.90)	(0.10)	(0.15)
			• •
PAni/HA/TiO <sub>2</sub> /C <sub>60</sub> (20 %)	1.00	10	20
	(0.90)	(0.10)	(0.20)
	1.00	10	40
PANI/HA/1102/C60 (40 %)	1.00	10	40
	(0.90)	(0.10)	(0.40)

Table 3.2: Synthesis of PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> with different contents of C<sub>60</sub>

## 3.4 Characterizations of PAni nanocomposites

## 3.4.1 Fourier Transform Infra-red (FTIR) Spectrometer

FTIR spectroscopy is an effective technique used to determine the functional groups of material in the range of mid IR region from 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup>. In general, every functional group will absorb different specific frequency IR radiation (Madejova, 2003).

In this study, FTIR analysis of fullerene doped PAni nanocomposites were recorded using the Perkin Elmer RX1 model spectrometer. PAni nanocomposites powders were grinded into the fine powder and dried overnight in oven before FTIR measurement. Small amount of PAni nanocomposites powder was added into the potassium bromide (KBr) powder with the ratio (PAni : KBr = 1 : 10) and then were grinded by using agitate mortar and pestle. The fine powder was distributed well in the mould and pressed to obtain a transparent, thin and uniform pellet. PAni nanocomposites in KBr pressed pellet were interpreted by using FTIR spectroscopy with wavenumber range from 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup> at room temperature.

## 3.4.2 Ultraviolet-visible (UV-Vis) Spectrometer

UV-Vis absorption spectroscopy is to study the electronic transition of molecules in ultraviolet-visible range from 300 nm to 900 nm. In principle of UV-Vis analysis, molecules will be exposed to the light of ultraviolet and visible radiation, the electron of molecules will be promoted from lower energy state to the higher energy molecular orbital (Brown et al., 2009). The optical spectrometer of UV-Vis will record the wavelength at which absorption occurs and the spectrum of UV-Vis will be presented in the graph of absorbance versus wavelength.

The UV-Vis analysis of fullerene doped PAni nanocomposites was recorded by Shimadzu UV-1650 PC model. For the sample preparation, 0.005 g of PAni was dispersed in methanol under ultrasonic action for few hours in order to obtain a homogenous solution. In a meantime, the UV-Vis instruments was turned on and warmed up for approximately 15 minutes. Then, PAni nanocomposites in methanol solutions were transferred into cuvette for UV-Vis analysis from 300 nm to 900 nm at ambient temperature.

#### 3.4.3 X-ray Diffractometer (XRD)

The X-ray diffraction is an effective technique used for phase description of a crystalline compound and atomic spacing. Generally, XRD consists of three basic

components such as x-ray tube, sample holder and x-ray detector. During XRD analysis, X-ray beam of radiation will interact with the sample and produced the X-ray diffraction patterns. The diffraction rays are produced based on the angle between incident and diffracted rays (Stanjek & Hausler, 2004).

For the sample preparation, fullerene doped PAni powder was distributed well in a steel plate sample holder. The XRD patterns of PAni nanocomposites was recorded by the Siemens D500 model at room temperature. The amorphous behavior of PAni nanocomposites were identified using Cu Ka (Ka = 1.54056 Å) at 35 kV and the results obtained were in the 20 range of 5° - 80° with scanning speed of 0.1°/min.

#### **3.4.4 Field Emission Scanning Electron Microscope (FESEM)**

FESEM is an analytical technique used to observe the surface structure as small as 1 nm, composition and type of the sample. Basically, the beam electron is emitted through electron gun (sources of electron) and hit the surface of the sample. As a result, the secondary electron will release from the surface of the sample and will be caught by detector to produce an electronic signal that can be converting into images at monitor (Gnanamoorthy et al., 2013).

For the sample preparation, fullerene doped PAni powder was distributed evenly on the surface of conductive tape that stacked on the sample holder. Then, the sample holder was placed into the FESEM instrument (JEOL JSM-7600F model). The FESEM images obtained were captured with magnification of 30,000 x at room temperature.

#### **3.4.5** Electrical conductivity

The electrical conductivities of PAni nanocomposites were tested by four-point probe method using resistivity meter (Loresta-GP MCP-T610) model at room temperature. Basically, PSP probe were used for measure small sample in circular or rectangular shape. This probe has 4 point pins as shown in Figure 3.2, where constant current (I) were applied through outer two pin probes (1 and 4), while the voltage (V) were flowed through the inner two pin probes (2 and 3). The inner pin distance for PSP probe is 1.5 mm.



Figure 3.2: Electrical conductivity of PAni nanocomposites in pellet form was measured by using PSP probe

For the sample preparation, fine powder of fullerene doped PAni nanocomposites were dried overnight in oven. Then,  $\sim 0.085$  g of PAni powder were distributed evenly in pellet mould and compressed slowly by a constant load of 625 kg

for 10 minutes. The electrical conductivity of PAni nanocomposites in pellet form with the diameter of 10 mm, thickness of ~ 1 mm and densities of ~1.00 g/cm<sup>3</sup> were measured by four-point probe (PSP probe) for five times and the average conductivities of PAni nanocomposites were calculated.

#### **3.4.6** Microwave absorption measurement

The microwave absorption properties of PAni nanocomposites were measured by Microwave Vector Network Analyzer (MVNA) from frequency range of 0.5 GHz to 18.0 GHz. The two ports devices that consist of complex reflection and transmission characteristics can be measured by MVNA, in which the incident signal was measured, dividing the reflected and transmitted waves following by displayed the ratio that are directly proportional to the reflection and transmission coefficient. Nevertheless, one port devices by metal-backed system were used in this study.

Full cycle of one-port calibration was carried out before measurement in order to minimize an error during microwave measurement such as load match, isolation, source match, directivity and frequency response. MVNA was calibrated by using air as standard where  $\varepsilon_{r}' = 1$ ,  $\varepsilon_{r}'' = 0$ ,  $\mu_{r}' = 1$  and  $\mu_{r}'' = 0$  in frequency range of 0.5 GHz to 18 GHz. The complex scattering parameters corresponded to reflection S<sub>11</sub>\* of transverse electromagnetic (TEM) were determined which commit on a model of single-layered plane wave absorber backed by an excellent conductor (Ferrero & Pirola, 2006). Thus, transmission of microwave was expected 0 %. Besides, the complex dielectric permittivity ( $\varepsilon_{r}^* = \varepsilon_{r}' - \varepsilon_{r}''$ ) and complex magnetic permeability ( $\mu_{r}^* = \mu_{r}' - \mu_{r}''$ ) were studied which consist of real part ( $\varepsilon_{r}'$  or  $\mu_{r}''$ ) which known as storage capability for EM wave energy and imaginary part ( $\varepsilon_{r}''$  or  $\mu_{r}''$ ) of dielectric permittivity and magnetic permeability which also known as loss capability for EM wave energy (Yusoff et al., 2002). For the sample preparation, ~0.1 g of PAni powder were placed evenly in toroidal mould as shown in Figure 3.3 (a). Then, the samples of PAni nanocomposites were compressed up to 750 kg for 30 minutes and the densities of the samples were ~1.10 g/cm<sup>3</sup>. The toroidal samples of PAni nanocomposites with outer diameter of 6.92 - 6.94 mm, inner diameter of 2.8 mm and thickness of 2.6 – 2.7 mm (Figure 3.2 (b)) were measured for microwave absorption from frequency range of 0.5 GHz to 18 GHz by MVNA (Anritsu 37369C model) as shown in Figure 3.4. The reflection (RL) and loss tangent (tan  $\delta$ ) of the PAni nanocomposites were calculated by using formula, RL = 20 log S<sub>11</sub><sup>\*</sup> and tan  $\delta = \varepsilon_r''/\varepsilon_r'$ , respectively.





Figure 3.3: (a) Toroidal mould and (b) toroidal sample used for MVNA measurement



Figure 3.4: MVNA instrument of Anritsu 37369 C model used for microwave measurement

#### **CHAPTER 4: RESULTS AND DISCUSSIONS**

#### 4.1 PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> nanocomposites without and with chemical treatment

#### 4.1.1 Characterization of PAni (without and with chemical treatment)

#### (a) FTIR analysis

Figure 4.1 (a) – (f) displays the FTIR spectra of pristine  $C_{60}$ , PAni (PAni/HA/TiO<sub>2</sub>), fullerene doped nanocomposites PAni nanocomposites  $(PAni/HA/TiO_2/C_{60})$  without and with chemical treatment by using different types of sulfonic groups (AOT, DBSA and CSA) for comparison purpose. In general, pristine PAni nanocomposites (Figure 4.1 (b)) and fullerene doped PAni nanocomposites without (Figure 4.1 (c)) and with chemical treatment (Figure 4.1 (d) - (f)) shows similar FTIR pattern. The characteristic peaks at  $1576.02 \text{ cm}^{-1} - 1578.45 \text{ cm}^{-1}$  and  $1494.15 \text{ cm}^{-1}$ <sup>1</sup> - 1497.03 cm<sup>-1</sup> are corresponding to the stretching vibration of quinoid (C=N) and benzenoid (C=C) rings, respectively. The C-N stretching of secondary aromatic amine and C-N<sup>+</sup> stretching in polaron form were shown by the bands at 1301.01 cm<sup>-1</sup> -1310.08 cm<sup>-1</sup> and 1245.11 cm<sup>-1</sup> - 1250.25 cm<sup>-1</sup>, respectively (Xiong et al., 2012).

The IR peaks at 1174.57 cm<sup>-1</sup> - 1178.36 cm<sup>-1</sup> are represented by the stretching vibration of  $-NH^+$  in benzenoid- $NH^+$ -quinoid segment in bipolaron forms. The peak range between 821.01 cm<sup>-1</sup> – 825.18 cm<sup>-1</sup> could be assigned to the aromatic C-H out of plane deformation vibration for 1, 4- disubstituted in benzene rings. The long absorption tail above ~1700 cm<sup>-1</sup> is corresponding to the high electrical conductivity due to the high degree of electron delocalization of PAni. As conclusion, all the FTIR spectra for both PAni nanocomposites and fullerene doped PAni nanocomposites have shown similar characteristics peaks with pristine PAni (PAni/HA) as reported by Phang and co-workers because the addition of TiO<sub>2</sub> and C<sub>60</sub> do not affect the chemical structure of PAni (Phang et al., 2008).

For fullerene doped PAni nanocomposites (Figure 4.1 (c) – (f)), the characteristic bands of  $C_{60}$  can be found at the peak of 526.11 cm<sup>-1</sup> and 576.35 cm<sup>-1</sup> which is similar with pristine  $C_{60}$  (Figure 4.1 (a)) (Wang et al., 2012). However, a small shift in the characteristic bands for fullerene doped PAni nanocomposites (without and with treated) at 1301.01 cm<sup>-1</sup> and 1245.11 cm<sup>-1</sup> can be observed as compared to PAni nanocomposites (PAni/HA/TiO<sub>2</sub>) (1310.08 cm<sup>-1</sup> and 1250.25 cm<sup>-1</sup>) due to the intermolecular interaction between PAni and C<sub>60</sub> during polymerization (Frackowiak & Beguin, 1995).



**Figure 4.1:** FTIR spectra of (a) pristine  $C_{60}$ , (b) pristine PAni (PAni/HA/TiO<sub>2</sub>), (c) PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> (without chemical treatment), (d) PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> (treated with AOT, (e) PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> (treated with DBSA) and (f) PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> (treated with CSA

#### (b) UV-Vis analysis

Figure 4.2 represents the UV-vis spectrum of PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> (treated with CSA) nanocomposites. UV-Vis spectra for PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> (without chemical treatment), PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> (treated with AOT) and PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> (treated with DBSA) nanocomposites were shown in Appendix A1-A3. In general, all fullerene doped PAni nanocomposites without and with chemical treatment (sulfonic group) revealed almost indistinguishable peak in the UV-vis spectra from 300 nm to 900 nm.

Basically, all PAni nanocomposites (without and with treatment) possess 3 majors absorption band at 375 nm, 464 nm and 800 nm. The absorption bands at 375 nm shows the  $\pi$ - $\pi$ \* transition of the benzenoid to quinoid ring while the shoulder-like peak at 464 nm indicates the bipolaron peak of PAni. Besides, free carriers tail at 800 nm represent the  $\pi$ -polaron transition of that indicates PAni is in conducting behavior (Phang et al., 2008).



Figure 4.2: UV-Vis spectrum of  $PAni/HA/TiO_2/C_{60}$  nanocomposites (treated with CSA)

#### (c) XRD analysis

The x-ray diffraction patterns of PAni/HA/TiO<sub>2</sub>, PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> nanocomposites without and with chemical treatment by different types of sulfonic groups such as AOT, DBSA and CSA were shown in Figure 4.3. Referring to the Figure 4.3 (a) – (e), all PAni nanocomposites shows almost alike X-ray diffraction pattern. The characteristic peaks of PAni at  $2\theta = 25.4^{\circ}$  and  $28.5^{\circ}$  which is associated to the periodicity parallel and perpendicular of the chain direction of PAni chain shows similar XRD pattern with pristine PAni (PAni/HA) as shown in Appendix B4 (Mo et al., 2007).

On the other hand, the sharp crystalline TiO<sub>2</sub> peaks at  $2\theta = 25.4^{\circ}$ ,  $36.1^{\circ}$ ,  $37.9^{\circ}$ ,  $48.1^{\circ}$ ,  $54.9^{\circ}$ ,  $62.8^{\circ}$ ,  $69.1^{\circ}$  and  $75.1^{\circ}$  significantly confirmed by the similar XRD pattern of pure TiO<sub>2</sub> as shown in Appendix B1 (Xia, & Wang, 2002). Figure 4.3 (b-e) shows the sharp crystalline peaks of C<sub>60</sub> at  $2\theta = 10.8^{\circ}$ ,  $17.9^{\circ}$  and  $21.1^{\circ}$  as compared with Figure 4.3 (a). Besides, the sharp crystalline peaks of C<sub>60</sub> at  $2\theta = 10.8^{\circ}$ ,  $17.9^{\circ}$  and  $21.1^{\circ}$  were significantly proven by the similar XRD pattern of pristine C<sub>60</sub> as shown in Appendix B2 (Politakos et al., 2013).

The X-ray diffraction patterns of all fullerene doped PAni nanocomposites exhibited the similar characteristic peaks of pristine PAni/HA, TiO<sub>2</sub> and C<sub>60</sub> without any shift, which validated the existing of TiO<sub>2</sub> and C<sub>60</sub> in the fullerene doped PAni nanocomposites. Hence, it can be suggested that the addition of dielectric and carbonaceous materials such as TiO<sub>2</sub> and C<sub>60</sub> did not affect the chemical structure of fullerene doped PAni nanocomposites.

As summary, FTIR, UV-Vis and XRD spectra for all fullerene doped PAni nanocomposites had confirmed that the resulting PAni is in the emeraldine salt form, which is electrically conducting with the existing of C<sub>60</sub> and TiO<sub>2</sub>.



**Figure 4.3:** X-ray diffraction patterns of (a) PAni/HA/TiO<sub>2</sub>, (b) PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> (without treated), (c) PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> (treated with AOT), (d) PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> (treated with DBSA) and (e) PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> (treated with CSA)

## (d) Morphology behaviors

Figure 4.4 represents the FESEM images of PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> nanocomposites (without and with chemical treatment by sulfonic groups: AOT, DBSA and CSA) with magnification of 30,000 x. As shown in Figure 4.4 (a), it was clearly observed that PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> nanocomposites without chemical treatment shows an agglomeration of particle. It is because of C<sub>60</sub> without chemical treatment will agglomerate to each other easily, thus it will act as the barrier for the formation of micelles that might produce the nanorods/nanotubes through elongation. This phenomenon can be explained by the proposed mechanism as shown in Figure 4.5 (a). During polymerization, most of the TiO<sub>2</sub> and C<sub>60</sub> will agglomerate together and formed the nanoparticles. On the other hand, some of the TiO<sub>2</sub> and C<sub>60</sub> were wrapped by the PAni/HA in which  $TiO_2$  and  $C_{60}$  was acting as the core of the nanoparticle individually.

However, PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> nanocomposites treated by sulfonic groups such as AOT, DBSA and CSA significantly induced the formation of nanorods/nanotubes with diameter (D) of 90 nm, 100 nm and 200 nm , respectively (Figure 4.4 (b) – (d)). The main function of the sulfonic groups (AOT, DBSA and CSA) is to enhance the dispersion of C<sub>60</sub> in Ani/HA/TiO<sub>2</sub> solution. It is because the SO<sub>3</sub><sup>-</sup> that surround the C<sub>60</sub> will cause the common ion effect, thus prevent the aggregation of C<sub>60</sub> (Dai et al., 1998). This has significantly proven that the chemical treatment by sulfonic groups could prevent the agglomeration of C<sub>60</sub> in PAni nanocomposites, thus improving the dispersion of C<sub>60</sub> that might induce the micelle formation, finally producing larger amount of nanorods/nanotubes.



(a) PAni/HA/TiO2/C 50 (without treated)



(c) PAni/HA/TiO2/C50 (treated with DBSA)



(b) PAni/HA/TiO2/C60 (treated with AOT)



(d) PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> (treated with CSA)

**Figure 4.4:** FESEM images for (a)  $PAni/HA/TiO_2/C_{60}$  (without treated), (b)  $PAni/HA/TiO_2/C_{60}$  (treated with AOT), (c)  $PAni/HA/TiO_2/C_{60}$  (treated with DBSA) and (d)  $PAni/HA/TiO_2/C_{60}$  (treated with CSA) (scale 0.5 cm = 100 nm)

In practice, the formation of nanorods/nanotubes for fullerene doped PAni nanocomposites (Figure 4.4 (b) – (d)) can be explained by the suggested mechanism as shown in Figure 5.4 (b). The medium during polymerization on this research study is water. Referring to the suggested mechanism, it was proposed that  $TiO_2$  and  $C_{60}$  were present as the nucleus of the micelles individually due to the better dispersion of  $TiO_2$  and  $C_{60}$  in the Ani/HA solution. Besides, Ani will act as the head (shell) of the micelle due to hydrophobic property of Ani monomer. On the other hand, HA will act as the tail of the micelle due to the hydrophilic of –COOH group in HA dopant.

Since, Ani/HA/TiO<sub>2</sub>/C<sub>60</sub> micelles were polymerized under uninterrupted condition, thus Ani/HA/TiO<sub>2</sub>/C<sub>60</sub> micelles will polymerize through the elongation at the micelle/water interface in order to form nanorods/nanotube of the fullerene doped PAni nanocomposites. Polymerizations of these PAni nanocomposites were proceeding in the micelle/water interface due to the hydrophilicity of APS as an oxidant. The suggested mechanism in this study is comparable to the Ani/HA/TiO<sub>2</sub> micelles mechanism as reported by Zhang and co-workers (Zhang et al., 2005). Predominantly, the formation of nanorods/nanotubes depends on the synthesis parameter such as the types of dopant, concentration of filler, temperature of polymerization and so on (Wan, 2008).

Among all sulfonated treated fullerene doped PAni, PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> (treated with CSA) has produced the largest amount of nanorods/nanotubes with D of 200 nm as shown in Figure 4.1 (d). This phenomenon happened because CSA possess the shortest alkyl groups with less steric hindrance, thus inducing a better dispersion of C<sub>60</sub> to form more Ani/HA/TiO<sub>2</sub>/C<sub>60</sub> micelles through elongation during polymerization as compared to other sulfonic groups (AOT and DBSA) that possess the longer alkyl chain with higher steric hindrance. The formation of more micelles that initiated by CSA will

significantly produce larger amount of nanorods/nanotubes through elongation at micelle/water interface.



**Figure 4.5:** Proposed mechanism for the formation of  $PAni/HA/TiO_2/C_{60}$  nanocomposites (a) without and (b) with chemical treatment by sulfonic groups

#### (e) Electrical conductivity studies

The electrical conductivities of PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> nanocomposites without and with chemical treatment by sulfonic groups (AOT, DBSA and CSA) were shown in Figure 4.6. Based on the result obtained, fullerene doped PAni nanocomposites with chemical treatment shows higher conductivity ( $8.218 \times 10^{-2} - 1.708 \times 10^{-1}$  S/cm) as compared to those without chemical treatment ( $3.655 \times 10^{-2}$  S/cm). Basically, the electrical conductivities of PAni relied on the doping level, conjugated or chain length, interchain and intrachain distance and external factors such as orientation of particles (Feng, et al., 2003).

PAni nanocomposites with chemical treatment shows a good dispersion during synthesis of PAni due to the common effect of  $SO_3^-$  that surrounds the  $C_{60}$  as compared to that without chemical treatment. In this research work, PAni can be considered as a good electron donor, while the  $C_{60}$  is a relatively good electron acceptor (Frackowiak &

Beguin, 1996). A good dispersion of  $C_{60}$  (with chemical treatment) might have acted as a good electron acceptor to withdraw more electrons from PAni backbone to form more extra holes (carbocation). Thus, it will significantly improve the amount of charge carriers (holes) along PAni chain and ultimately increase the electrical conductivity of PAni nanocomposites by comparing with those without chemical treatment.

Among all fullerene doped PAni nanocomposites with chemical treatment, PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> (treated with CSA) possesses the highest electrical conductivity  $(1.708 \times 10^{-1} \text{ S/cm})$  due to the better dispersion of C<sub>60</sub> with CSA during polymerization of PAni. The better dispersion of fullerene (after chemical treatment) during polymerization will induce more the formation of nanorods/nanotubes that will enhance the electron movement between intrachain and interchain along the PAni backbone. Some of sulfonic groups left over in this PAni will create a barrier that block the conductivity pathway, however sulfonic groups (CSA) with the shortest alkyl group with the less steric hindrance induce lesser blockage for conductive pathway, thus possess the highest conductivity compared with those with AOT and DBSA treatment.

However, PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> (treated with DBSA and AOT), revealed the lower electrical conductivities  $(5.433 \times 10^{-2} - 8.218 \times 10^{-2} \text{ S/cm})$  among fullerene doped PAni nanocomposites with chemical treatment. It is because the long chain alkyl groups in DBSA and AOT will create more steric hindrance between PAni and C<sub>60</sub> that significantly blocked the movement of charge carrier between the intrachain and interchain of PAni, thus reducing the conductivities.



**Figure 4.6:** Electrical conductivities of PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> nanocomposites without and with treatment by sulfonic groups (AOT, DBSA and CSA)

# 4.1.2 Microwave absorption studies of PAni (without and with chemical treatment)

For the microwave absorption studies, the complex dielectric permittivity ( $\varepsilon_r^* = \varepsilon_r' - \varepsilon_r''$ ) and complex magnetic permeability ( $\mu_r^* = \mu_r' - \mu_r''$ ) of the samples were measured from frequency range of 0.5 GHz till 18.0 GHz using MVNA at room temperature. Generally, reflection loss (RL) is used to study the interaction between conducting particles in both conducting material and EM material. In this research work, the RL of fullerene doped PAni nanocomposites were calculated by using formula RL = 20 log S<sub>11</sub><sup>\*</sup>. Basically, the microwave absorbance of PAni nanocomposites can be anticipated from RL where the larger negative value of RL

possesses good microwave absorption of PAni nanocomposites that indicate a good EMI shielding efficiency (Yang et al., 2016).

Figure 4.7 shows the RL of fullerene doped PAni nanocomposites without and with chemical treatment by different types of sulfonic groups (AOT, DBSA and CSA). Based on Figure 4.7, it can be clearly determined that the fullerene doped PAni nanocomposites with chemical treatment exhibited narrow and sharp RL peak from - 53.0 dB to -61.3 dB in the frequency range of 7-11 GHz that show a good absorption. By comparison, the fullerene doped PAni nanocomposites without chemical treatment exhibited the broad RL peak of -37.2 dB at frequency 9 GHz which indicated a poor absorption. Among all fullerene doped PAni nanocomposites with chemical treatment, PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> (treated with CSA) possessed the narrow and highest RL peak of -61.3 dB that showed the strongest EMI shielding efficiency.



**Figure 4.7:** RL for PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> nanocomposites without and with treatment by sulfonic groups (AOT, DBSA and CSA)

The loss tangent (tan  $\delta$ ) of fullerene doped PAni nanocomposites without and with chemical treatment as shown in Figure 4.8 were calculated from the real and imaginary parts of complex dielectric permittivity by using formula tan  $\delta = \varepsilon_r''/\varepsilon_r'$ . Basically, the strong absorption (higher negative value of RL) as well as a good EMI shielding efficiency of fullerene doped PAni nanocomposites can be determined by the higher tan  $\delta$  of PAni nanocomposites. Referring to Figure 4.8, fullerene doped PAni nanocomposites with chemical treatment revealed a higher tan  $\delta$  (0.46 - 0.38) which were acknowledged as lossy material that possess strong absorption as compared to those without chemical treatment that shows similar trend with RL as shown in Figure 4.7. Similarly, the highest tan  $\delta$  of fullerene doped PAni (treated with CSA) that obtained from Figure 4.8 also strongly manifest by the highest RL as shown in Figure 4.7.



**Figure 4.8:** The loss tangent (tan  $\delta$ ) for fullerene doped PAni nanocomposites without and with treatment by sulfonic groups (AOT, DBSA and CSA)

The dielectric permittivity ( $\varepsilon_r'$ ) of PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> nanocomposites without and with chemically treated by sulfonic groups were shown in Figure 4.9. Based on the data obtained, PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> nanocomposites with chemical treatment exhibited the higher  $\varepsilon_r'$  (0.46 – 0.38) as compared to those without chemical treatment (0.37). Among all fullerene doped PAni with chemical treatment, PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> (treated with CSA) possesses the highest  $\varepsilon_r'$  (0.46).

Predominantly,  $\varepsilon_r'$  of PAni nanocomposites depends on several factors such as electronic, ionic, orientation and space charge polarization (heterogeneity) (Hamid et al., 2002). In this study, fullerene doped PAni with chemical treatment significantly improved the dispersion of C<sub>60</sub> which will enhance the orientation and space charge polarization along the PAni backbone, thus increasing the  $\varepsilon_r'$  as compared with those without chemical treatment.

Referring to the FESEM images of PAni nanocomposites in Figure 4.4, fullerene doped PAni with chemical treatment that possess higher amount of nanorods/nanotubes significantly enhanced the heterogeneity of the PAni. The highest heterogeneity of PAni subsequently improved the space polarization as well as the  $\varepsilon_r'$  of PAni. Thus, it can be observed that the trend for the amount of nanorods/nanotubes as shown in Figure 4.4 is tally with the  $\varepsilon_r'$  trend of PAni in Figure 4.9.



**Figure 4.9:** Dielectric permittivity ( $\epsilon_r$ ) for PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> without and with treatment by sulfonic groups (AOT, DBSA and CSA)

By combining all the parameters as discussed earlier, fullerene doped PAni with chemical treatment that possessed the higher  $\varepsilon_r'$  (0.46 – 0.38), heterogeneity (amount of nanorods/nanotubes) and electrical conductivity (8.218 × 10<sup>-2</sup> – 1.708 × 10<sup>-1</sup> S/cm) will induce more molecular polarization along the PAni chain. Thus, it will significantly activate more current when the incidents of EM wave pierce the surface of PAni. Finally, the electrical energy which is dissipated by fullerene doped PAni with chemical treatment will notably enhance the EMI shielding properties of PAni nanocomposites (RL from -53 dB to -61.3 dB) as compared with those without chemical treatment (RL = -37.2 dB).

Among all fullerene doped PAni with chemical treatment, PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> nanocomposites (treated with CSA) revealed the highest  $\varepsilon_r$ ' (0.46), heterogeneity (larger amount of nanorods/nanotubes) and electrical conductivity (1.708 × 10<sup>-1</sup> S/cm) that induce more disordered motion of charge carrier along the backbone of PAni. Thus, it

will exhibit greater molecular polarization phenomena such as greater space charge relaxation, dipole rotation and hopping of confined charges. Finally,  $PAni/HA/TiO_2/C_{60}$  (treated with CSA) will significantly enhance the RL of -61.3 dB at 9 GHz with excellent EMI shielding properties.

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## 4.2 PAni nanocomposites with different types of fullerene (C<sub>60</sub> and S.G.F)

Based on the previous data obtained for fullerene doped PAni nanocomposites without and with chemical treatment by sulfonic groups (AOT, DBSA and CSA) as shown in Part 4.1, fullerene doped PAni with chemical treatment by CSA possesses the best EMI shielding properties with the highest RL of -61.3 dB at 9 GHz. Basically, the largest negative value of RL for fullerene doped PAni with chemical treatment by CSA (-61.3 dB) might indicate the highest absorption of the material, which eventually will perform a good effectiveness of EMI shielding properties. Thus, PAni nanocomposites with chemical treatment by CSA was continued for the proceeding part without and with addition of different types of fullerene.

### 4.2.1 Characterization of PAni with different types of fullerene

## (a) FTIR analysis

Figure 4.10 demonstrated the FTIR spectra of PAni nanocomposites without and with addition of different types of fullerene (C<sub>60</sub> and S.G.F) that treated with CSA. Generally, all PAni nanocomposites without and with addition of fullerene possesses similar FTIR pattern from 4000 cm<sup>-1</sup> – 400 cm<sup>-1</sup>. The characteristics bands of emeraldine salt PAni were observed in the spectra at 1574.25 – 1579.15 cm<sup>-1</sup> and 1495.60 – 1499.03 cm<sup>-1</sup> which indicating the quinoid nitrogen (C=N) deformation and benzenoid (C=C) stretching deformation of PAni nanocomposites, respectively. These characteristic bands were ascribed to the conducting state of the PAni.

805.74 cm<sup>-1</sup> could be assigned to the aromatic C-H out of plane deformation vibration for the p-disubstituted benzene rings.

Additionally, PAni with addition of fullerenes (Figure 4.9 (b) and (c)) shows the characteristic bands of fullerene at 526.15 cm<sup>-1</sup> and 576.21 cm<sup>-1</sup>. The addition of fullerene in PAni has small shifted the quinoid and benzenoid bands from 1553 cm<sup>-1</sup> and 1478 cm<sup>-1</sup> (PAni without addition of fullerenes) to higher wavenumber of 1574 cm<sup>-1</sup> and 1495 cm<sup>-1</sup> that significantly indicating the interaction between PAni and fullerenes. The peaks obtained in this study resemble the characteristic peak of PAni nanocomposites as described in literature as reported by Li and co-workers (Li, & Wan, 1995). Hence, the FTIR spectra obtained significantly manifests the functional groups of PAni nanocomposites.



Figure 4.10: FTIR spectra of (a)  $PAni/HA/TiO_2$ , (b)  $PAni/HA/TiO_2/C_{60}$  and (c)  $PAni/HA/TiO_2/S.G.F$ 

#### (b) UV-vis analysis

Figure 4.11 represents the UV-vis spectrum of PAni/HA/TiO<sub>2</sub>/C<sub>60</sub>, while the UV-Vis spectra of for both PAni/HA/TiO<sub>2</sub> and PAni/HA/TiO<sub>2</sub>/S.G.F were shown in Appendix A4 and A5, respectively. The UV-Vis spectra of PAni nanocomposites without and with addition of fullerenes (C<sub>60</sub> and S.G.F) treated by CSA shows identical peaks in the region 300 nm to 900 nm.

Based on Figure 4.11, PAni nanocomposites possess two absorption bands at 375 nm and 464 nm which indicates the  $\pi$ - $\pi$ <sup>\*</sup> transition of benzenoid ring to quinoid ring, and bipolaron behavior of PAni nanocomposites. Besides, a free carrier tail near 700 nm indicates the polaron behavior of PAni nanocomposites, which shows that PAni was in the conducting state (Kocherginsky & Wang, 2006).



Figure 4.11: UV-vis spectrum of PAni/HA/TiO<sub>2</sub>/C<sub>60</sub>

#### (c) XRD analysis

The X-ray diffraction patterns of PAni nanocomposites without and with addition of fullerene that treated with CSA were shown in Figure 4.12. Generally,  $PAni/HA/TiO_2/C_{60}$  and  $PAni/HA/TiO_2/S.G.F$  as shown in Figure 4.12 (b) and (c) possess almost identical diffraction patterns as compared to those without addition of fullerene (Figure 4.12 (a)).

The diffraction patterns of doped PAni for all PAni nanocomposites were presented at peaks  $2\theta = 25.0^{\circ} - 28.5^{\circ}$  due to the periodicity parallel and perpendicular of the polymer chain direction of PAni. The presence of TiO<sub>2</sub> in all PAni nanocomposites was determined by the characteristic peaks at  $2\theta = 27.6^{\circ}$ ,  $37.9^{\circ}$ ,  $48.2^{\circ}$ ,  $54.1^{\circ}$ ,  $55.3^{\circ}$ ,  $62.8^{\circ}$ ,  $68.9^{\circ}$ ,  $70.4^{\circ}$  and  $75.2^{\circ}$ . Besides, the peaks at  $27.6^{\circ}$  and  $37.9^{\circ}$  that assigned to the 101 and 004 reflections of anatase significantly confirmed that TiO<sub>2</sub> used on the anatase form (Sakurai & Mizusawa, 2010). On the other hand, it can be clearly access that the peaks for the existence of C<sub>60</sub> for PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> and PAni/HA/TiO<sub>2</sub>/S.G.F were located at  $2\theta$ = 18.5° and 21.3° with the reflections of (110) and (220), respectively as shown in Figure 4.12 (b) and (c), respectively (Ginzburg et al., 2005).

The X-ray diffraction patterns of PAni nanocomposites exhibited the characteristic peaks of PAni,  $TiO_2$  and  $C_{60}$  that validated the existing of  $TiO_2$  and  $C_{60}$ . Therefore, it can be suggested that the addition of different types of fullerene ( $C_{60}$  and S.G.  $C_{60}$ ) and  $TiO_2$  does not affect the chemical structure of PAni nanocomposites. In summary, FTIR, UV-Vis and XRD spectra as shown in Figure 4.10, 4.11 and 4.12 revealed the successful synthesis of PAni nanocomposites.


**Figure 4.12:** X-ray diffraction patterns of PAni nanocomposites (a) PAni/HA/TiO<sub>2</sub>, (b) PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> and (c) PAni/HA/TiO<sub>2</sub>/S.G.F

## (d) Morphology behaviors

Figure 4.13 displays the FESEM images of PAni nanocomposites without and with addition of fullerene ( $C_{60}$  and S.G.F) which treated by CSA with a magnification of 30,000 x. Generally, the FESEM images shows that all PAni nanocomposites successfully produced the nanorods/nanotubes through elongation.

Note that the D of nanorods/nanotubes for PAni nanocomposites without addition of fullerene (PAni/HA/TiO<sub>2</sub>; 160 nm) is smaller than those with addition of fullerene such as PAni/HA/TiO<sub>2</sub>/S.G.F (180 nm) and PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> (200 nm). Formation of the smallest D of nanorods/nanotubes (160 nm) for those without addition of fullerenes as shown in Figure 4.13 (a) was similar to the morphology and proposed mechanism as shown in Figure 4.5 (b) with TiO<sub>2</sub> as the nucleus of the micelle.

Oppositely, the addition of TiO<sub>2</sub> and fullerene with bigger D into the Ani/HA micelles significantly will produce PAni nanocomposites nanorods/nanotubes with bigger D.

Besides, it had been noticed that many bulk particle appeared around the nanorods/nanotubes for PAni/HA/TiO<sub>2</sub>/S.G.F as shown in Figure 4.13 (b). It is because S.G.F is a giant molecular structure that consists the mixture of fullerene from  $C_{60}$  to  $C_{84}$  with irregular shape. The addition of this giant molecular structure into Ani/HA micelles might create the steric hindrance during elongation process and hence led to the agglomeration of particles and thus blocked the polymerization of PAni through elongation. Besides, S.G.F with irregular shape might counteract to Ani/HA micelles that can distort the formation of nanorods/nanotubes. Thus, it significantly reduces the D of nanorods/nanotubes and induces the formation of more bulk particles.

Among all the PAni with addition of different types of fullerene, PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> shows the highest amount of nanorods/nanotubes with biggest D and less bulk particle. This phenomenon happened because the spherical C<sub>60</sub> and Ani/HA micelles were cooperated to each other easily due to the strong synergy effect that might eventually induce the formation of more nanorods/nanotubes with the biggest D.



**Figure 4.13:** FESEM images of (a) PAni/HA/TiO<sub>2</sub>, (b) PAni/HA/TiO<sub>2</sub>/S.G.F and (c) PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> [magnification; 30, 000 x; scale: 0.5 cm = 100 nm]

## (e) Electrical conductivity studies

The electrical conductivities of PAni nanocomposites without and with addition of fullerene (C<sub>60</sub> and S.G.F) that treated with CSA were shown in Figure 4.14. The conductivities of the PAni nanocomposites obtained in this study were following the descending order of PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> (1.708 × 10<sup>-1</sup> S/cm), PAni/HA/TiO<sub>2</sub> (1.439 ×  $10^{-2}$  S/cm) and PAni/HA/TiO<sub>2</sub>/S.G.F (4.531 ×  $10^{-3}$  S/cm). Basically, the shape of fullerene, fullerene content and crystallinity are the few factors that might affect the electrical conductivity of PAni (Politakos et al., 2013). However, both the shape and crystallinity of fullerene plays the main role in this research study in order to increase the conductivity of PAni. Based on Figure 4.14, for PAni nanocomposites with addition of fullerenes, PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> reveal the highest conductivities compared to PAni/HA/TiO<sub>2</sub>/S.G.F. This phenomenon can be explained by the schematic illustration for the charge transfer between PAni and fullerene as shown in Figure 4.15. The regular and spherical shape of C<sub>60</sub> is easily interact with PAni, thus significantly enhance the intrachain and interchain charge transfer between C<sub>60</sub> and PAni along the polymer backbone that leading to the highest conductivities (Figure 4.15 (a)) (Xiong et al., 2012).

However, the S.G.F with irregular shape (spherical and elongated) may act as a barrier between S.G.F (consists  $C_{60}$  to  $C_{84}$  and higher) and PAni that significantly hindered the interchain and intrachain charge transfer, thus decreased the conductivity (Figure 4.15 (b)). Besides, some S.G.F with larger size and irregular shape might decreased the energy of  $1s - \pi^*$  and caused the S.G.F become more graphitic in nature. This significantly reduced the degeneracy of electronic structure due to the lower symmetry of S.G.F with the bigger size (Politakos et al., 2013). Moreover, the aggregate bulk particle of S.G.F that surrounded the nanorods/nanotubes of PAni/HA/TiO<sub>2</sub>/S.G.F (Figure 4.12 (b)) will act as impediment that distort the PAni conductive pathways and reduce the motion of charge carriers along PAni chain that ultimately decreased the conductivity. The phenomenon that explained about intrachain and interchain between fullerenes ( $C_{60}$  and S.G.F) and PAni in this research study is strongly agreed with the proposed mechanism for the charge transfer between PAni/N,N-Dimethylformamide composites with different fullerene system ( $C_{60}$  and S.G.F) as reported by Politakos and co-workers (Politakos et al., 2013).



**Figure 4.14:** Electrical conductivities of PAni nanocomposites without and with addition of different types of fullerene ( $C_{60}$  and S.G.F)



**Figure 4.15:** Schematic illustration for the charge transfer between PAni with (a)  $C_{60}$  and (b) S.G.F

(Adopted from: Politakos, N., Zalakain, I., Fernandez d'Arlas, B., Eceiza, A., & Kortaberria, G. (2013). Optical, structural and electrical properties of Polyaniline systems doped with  $C_{60}$  and small gap fullerenes. Materials Chemistry and Physics, 142 (1), 387-394).

## 4.2.2 Microwave absorption studies of PAni with different types of fullerene

Figure 4.16 represent the RL for PAni nanocomposites without and with addition of fullerene (C<sub>60</sub> and S.G.F). The microwave absorbance of PAni nanocomposites can be anticipated from RL where the larger negative values of RL, the excellent the microwave absorption of PAni that indicate good EMI shielding. PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> exhibit the highest and narrow sharp RL peak of -61.3 dB with best EMI shielding properties as compared to the PAni/HA/TiO<sub>2</sub>/S.G.F and PAni/HA/TiO<sub>2</sub> with the broad RL peak of -9.3 dB and -9.9 dB, respectively.



Figure 4.16: RL for PAni nanocomposites without and with addition of fullerene

Tan  $\delta$  of PAni nanocomposites without and with addition of fullerenes (C<sub>60</sub> and S.G.F) that treated by CSA is shown in Figure 4.17. Based on the result obtained, PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> displays the highest tan  $\delta$  (0.38) as compared to PAni/HA/TiO<sub>2</sub> (0.25) and PAni/HA/TiO<sub>2</sub>/S.G.F (0.24).

PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> displays the highest tan  $\delta$  because this PAni nanocomposites are acknowledge as lossy material that express a strong absorption that could point out the microwave absorbance. In general, both RL and tan  $\delta$  of PAni nanocomposites without and with addition of fullerenes (C<sub>60</sub> and S.G.F) shows the similar trend as shown in Figure 4.16 and Figure 4.17, respectively. Thus, the estimation microwave absorbance of PAni nanocomposites based on the highest tan  $\delta$  (0.38) of PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> as shown in Figure 4.17 are similar as the highest negative values of RL (-61.3 dB) as shown in Figure 4.16 that indicates strong absorption with best EMI shielding efficiency.



Figure 4.17: The loss tangent (tan  $\delta$ ) of PAni nanocomposites without and with addition of fullerene (C<sub>60</sub> and S.G.F)

The dielectric permittivity ( $\varepsilon_r'$ ) of PAni nanocomposites without and with addition of fullerenes (C<sub>60</sub> and S.G.F) that treated with CSA was shown in Figure 4.18. The  $\varepsilon_r'$  of PAni nanocomposites without and with fullerenes followed the descending order of PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> (10.1), PAni/HA/TiO<sub>2</sub>/S.G.F (5.8), PAni/HA/TiO<sub>2</sub> (5.5). The highest  $\varepsilon_{r}$ ' of PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> depends on the space-charge polarization that caused by the largest amount of nanorods/nanotubes (Figure 4.12 (c)) which indicates the highest heterogeneity of PAni nanocomposites. On the other hand, PAni/HA/TiO<sub>2</sub>/S.G.F with the lowest heterogeneity that caused by the fewer amounts of nanorods/nanotubes (Figure 4.12 (b)) due to the steric hindrance of large molecule of S.G.F will reduced the space charge polarization as well as the  $\varepsilon_{r}$ '.



**Figure 4.18:** Dielectric permittivity ( $\epsilon_r$ ') of PAni nanocomposites without and with addition of fullerene (C<sub>60</sub> and S.G.F)

In this study, among PAni without and with addition of fullerene, PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> revealed a good EMI shielding properties with the highest RL of -61.3 dB due to several factors such as the highest dielectric permittivity (10.1), the largest amount of nanorods/nanotubes and the highest electrical conductivities (1.708  $\times$  10<sup>-1</sup> S/cm) that will lead to a more disordered motion of charge carriers along the PAni backbone and exhibit the greater molecular polarization. Therefore, it will significantly induce higher current when incident EM waves penetrate the surface of PAni. Finally, the electrical energy dissipated by PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> could be enhanced and significantly elevates the microwave absorption with the highest RL (-61.3 dB), thus possess the best EMI shielding efficiency.

## 4.3 PAni nanocomposites with different contents of C<sub>60</sub>

Based on previous result obtained for PAni without and with addition for different types of fullerenes ( $C_{60}$  and S.G.F) as shown in Part 4.2, the addition of  $C_{60}$  into PAni nanocomposites with chemical treatment by CSA revealed the best EMI shielding properties with the highest RL of -61.3 dB. Thus, in this part,  $C_{60}$  doped PAni nanocomposites that treated with CSA were proceed with different contents of  $C_{60}$  (5%, 10%, 15%, 20% and 40%) for further study.

# 4.3.1 Characterization of PAni with different contents of C<sub>60</sub>

## (a) FTIR analysis

The FTIR spectra of pristine C<sub>60</sub>, pristine PAni and PAni nanocomposites that treated by CSA with different contents (5 %, 10 %, 15 %, 20 % and 40 %) of C<sub>60</sub> were shown in Figure 4.19. Generally, all PAni nanocomposites with different contents of C<sub>60</sub> possesses similar FTIR spectra pattern of pristine PAni (Figure 4.19 (b)) from 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup>. The functional groups of different contents of C<sub>60</sub> doped PAni was confirmed by FTIR spectra.

Based on FTIR spectra for all C<sub>60</sub> doped PAni nanocomposites as shown in Figure 4.19, the quinoid nitrogen C=N and benzenoid C=C stretching deformation can be detected at 1574.15 - 1576.35 cm<sup>-1</sup> and 1495.56 - 1498. 37 cm<sup>-1</sup>, respectively. The peak located at 1301.11 - 1301.20 cm<sup>-1</sup> and 1260.15 - 1263.56 cm<sup>-1</sup> were ascribed to the C-N<sup>+</sup> stretching vibration in polaron structure (Nikolaidis et al., 2016).

The characteristic vibration mode of quinoid unit in doped PAni was shown by the position at  $1121.24 - 1123.11 \text{ cm}^1$ . These were attributed to the charge transfer process in N atom that took place on the quinoid segment along the PAni chain. The peak at wavenumber range of 800.09 cm<sup>-1</sup> – 831.11 cm<sup>-1</sup> were represented the out of plane deformation of C-H on 1,4 – disubstituted of benzene rings. The peak at 526.15  $cm^{-1}$  - 576.06  $cm^{-1}$  was corresponding to the intramolecular modes of C<sub>60</sub> similar with pristine C<sub>60</sub> (Figure 4.19 (a)) (Sapurina et al., 2000).

The characteristics peak and functional groups of PAni nanocomposites obtained from FTIR analysis resemble those reported in literature. This indicates that PAni nanocomposites with different contents of  $C_{60}$  were successfully synthesized.



**Figure 4.19:** FTIR spectra of (a) pristine  $C_{60}$ , (b) PAni/HA/TiO<sub>2</sub>, (c) PAni with 5 % of  $C_{60}$ , (d) PAni with 10 % of  $C_{60}$ , (e) PAni with 15 % of  $C_{60}$ , (f) PAni with 20 % of  $C_{60}$  and (g) PAni with 40 % of  $C_{60}$ 

## (b) UV-vis analysis

Basically, all the UV-Vis spectra for different contents of  $C_{60}$  doped PAni nanocomposites show almost identical UV-Vis spectra in wavelength of 300 nm to 900 nm. Figure 4.20 represents the UV-Vis spectrum for 10 % of  $C_{60}$  doped PAni nanocomposites that treated with CSA. The UV-Vis spectra for others contents of  $C_{60}$  doped PAni were shown in Appendix A6 – A9.

As shown in Figure 4.20, three absorption bands of PAni nanocomposites can be observed at 375 nm, 464 nm and free carrier tail 700 nm. The two absorption bands at 375 nm and 700 nm shows the excitation of benzenoid segments to quinoid segments along the PAni chain and conducting behavior for emeraldine salt form of PAni nanocomposites, respectively. The shoulder like peak at 464 nm corresponds to the bipolaron peak of PAni (Kang et al., 2004).



Figure 4.20: UV-vis spectrum of PAni nanocomposites with 10 % of C<sub>60</sub>

## (c) XRD analysis

The result of crystallinity orientation for pristine C<sub>60</sub>, PAni/HA/TiO<sub>2</sub> and different contents of C<sub>60</sub> doped PAni that treated by CSA was shown in Figure 4.21. In general, all PAni nanocomposites with different contents of C<sub>60</sub> possessed almost alike X-ray diffraction patterns from  $2\theta = 5^{\circ}$  to 80°. Refer to Figure 4.21 (c) – (g), it can be clearly observe that the characteristic peaks for C<sub>60</sub> was located at  $2\theta = 18.5^{\circ}$  and  $21.3^{\circ}$  which is similar with pristine C<sub>60</sub> (Figure 4.21 (a)) (Giusca et al., 2002). There is an apparent increase in the intensity of C<sub>60</sub> peak with increasing contents of C<sub>60</sub> from 5 % (Figure 4.21 (c)) to 40 % (Figure 4.21 (g)) in the PAni nanocomposites.

For all PAni nanocomposites, the amorphous behavior of PAni at 20 range of  $25.0^{\circ}$  - 28.5° ascribed to the periodicity parallel and perpendicular of the PAni chain direction which is same as Figure 4.21 (b)). The crystallinity peaks at  $2\theta = 25.4^{\circ}$ ,  $36.1^{\circ}$ ,  $37.9^{\circ}$ ,  $48.1^{\circ}$ ,  $54.9^{\circ}$ ,  $62.8^{\circ}$ ,  $69.1^{\circ}$  and  $75.1^{\circ}$  were associated to the presence of TiO<sub>2</sub> in PAni nanocomposites (Radoicic et al., 2010).

Thus, the X-ray diffraction patterns for all PAni nanocomposites confirmed the existing of  $C_{60}$  and  $TiO_2$  along the PAni chain. In summary, it can be proposed that the addition of  $C_{60}$  and  $TiO_2$  do not influence the chemical structure of PAni because all PAni nanocomposites obtained show almost similar pattern for FTIR, UV-Vis and XRD spectra.



**Figure 4.21:** X-ray diffraction patterns of (a)  $C_{60}$ , (b) PAni/HA/TiO<sub>2</sub>, (c) PAni with 5 % of  $C_{60}$ , (d) PAni with 10 % of  $C_{60}$ , (e) PAni with 15 % of  $C_{60}$ , (f) PAni with 20 % of  $C_{60}$  and (g) PAni with 40 % of  $C_{60}$ 

## (d) Morphology behaviors

FESEM images in Figure 4.22 shows the morphology behavior of PAni nanocomposites that treated with CSA with different contents of  $C_{60}$  at magnification of 30,000 ×. It can be clearly observed that, all PAni nanocomposites with different contents of  $C_{60}$  have successfully formed the nanorods/nanotubes in D range of 170 nm - 200 nm.

Referring to Figure 4.21 (a) – (b), the increasing contents of  $C_{60}$  from 5 % to 10 % significantly increase both the amount and D of nanorods/nanotubes follow the ascending order of 170 nm – 200 nm. It is because the higher contents of  $C_{60}$  will induce the formation of more Ani/HA micelles, thus significantly produce more nanorods/nanotubes with the bigger D through elongation.

However, the increasing contents of  $C_{60}$  from 15 % to 40 % significantly decrease both the amount and D of nanorods/nanotubes follow the descending order of 180 nm – 120 nm (Figure 4.22 (c) – (e)). It is because the excess amounts of  $C_{60}$  (after the optimum contents of  $C_{60}$ ) will agglomerate and act as barrier that block the formation of micelles, thus reduce both the amount and D of nanorods/nanotubes. Among all PAni nanocomposites, PAni with 10 % of  $C_{60}$  is the optimum content that might produce the highest amount of nanorods/nanotubes with the biggest D of 200 nm (Figure 4.22 (b)) as compared to others.



(a) PAni/HA/TiO2/C60 (5%)/CSA



(d) PAni/HA/TiO2/C60 (20 %)/CSA

(e) PAni/HA/TiO2/C60 (40 %)/CSA



#### **(e) Electrical conductivity studies**

The electrical conductivities of PAni nanocomposites with different contents of C<sub>60</sub> that treated with CSA are tabulated in Figure 4.23. The conductivities of PAni nanocomposites with increasing contents of  $C_{60}$  from 5 % to 10 % shows the ascending

order from  $2.440 \times 10^{-2}$  S/cm to  $1.708 \times 10^{-1}$  S/cm. It is because the increasing contents of C<sub>60</sub> will induce not only more charge transfer interaction between PAni and C<sub>60</sub> but also the doping level along the PAni chain. Moreover, the increasing both the amounts and D of nanorods/nanotubes from 5 % to 10 % significantly improves the interchain and intrachain charge transfer along the PAni segments, thus increased the conductivities (Xiong et al., 2012).

On the other hand, the conductivities of PAni nanocomposites with continues increasing contents of C<sub>60</sub> (from 15 % to 40 %) possesses the descending order from  $4.828 \times 10^{-2}$  S/cm to  $2.692 \times 10^{-3}$  S/cm. This is because the excess C<sub>60</sub> will tend to agglomerates to each other and act as barrier that distort both the conjugation and coplanarity along PAni backbones, thus reduce conductivities. In conclusion, the decreasing both the amounts and D of nanorods/nanotubes from 15 % to 40 % significantly reduces the interchain and intrachain charge transfer along the PAni segments, thus reduced the conductivities.

Among all PAni nanocomposites, PAni with 10 % of C<sub>60</sub> possessed the highest electrical conductivities of  $1.708 \times 10^{-1}$  S/cm. The optimal content of C<sub>60</sub> (10 %) shows the best synergy interaction towards PAni that will induce more formation of polaron and significantly enhance the degree delocalization of electron along the PAni backbone (Sapurina et al., 2000; Wang et al.,2012). A good charge transfer of the optimal content of C<sub>60</sub> (10%) will led to the highest conductivity of PAni.



Figure 4.23: Electrical conductivities of PAni nanocomposites with different contents of  $C_{60}$ 

# 4.3.2 Microwave absorption studies of PAni with different contents of C<sub>60</sub>

Figure 4.24 shows the RL of PAni nanocomposites with different contents of  $C_{60}$  (5 %, 10 %, 15 %, 20 % and 40 %) that treated by CSA. It can be clearly determined that with increasing contents of  $C_{60}$  from 5 % to 10 %, RL of PAni was significantly increased from -42.1 dB to -61.3 dB. However, with continues increasing of  $C_{60}$  from 15 % to 40 %, RL of PAni was shows the descending order from -49.1 dB to -6.3 dB. Among all PAni nanocomposites, PAni with optimum  $C_{60}$  content (10 %), revealed the most narrow and sharpest RL peak (-61.3 dB) with the highest absorption that indicates the best EMI shielding properties.



**Figure 4.24:** RL of PAni nanocomposites with different contents of  $C_{60}$ : (a) 5 %, (b) 10 %, (c) 15 %, (d) 20 % and (e) 40 %

Generally, both RL and tan  $\delta$  as shown in Figure 4.24 and 4.25, respectively possesses similar trend in which RL with highest negative value will exhibit the highest tan  $\delta$  that indicate the strongest absorption as well as the best EMI shielding properties (Saini et al., 2009). Based on Figure 4.25, it can be determined that with increasing contents of C<sub>60</sub> from 5 % to 10 %, tan  $\delta$  shows the ascending order from 0.24 to 0.33 (Figure 4.25 (a) – (b)). However, tan  $\delta$  shows the descending order from 0.28 to 0.11 after continues addition of C<sub>60</sub> from 15 % to 40 % as shown in Figure 4.25 (c) – (e). Similarly, among all the PAni, PAni with 10 % of C<sub>60</sub> that possessed the highest tan  $\delta$ (0.33) indicates that this PAni is the lossiest materials that possess the highest microwave absorption with the best EMI shielding behavior.



**Figure 4.25:** Loss tangent of PAni nanocomposites with different contents of  $C_{60}$ : (a) 5 %, (b) 10 %, (c) 15 %, (d) 20 % and (e) 40 %

Figure 4.26 shows the  $\varepsilon_r'$  for PAni nanocomposites with different contents of C<sub>60</sub> (5 %, 10 %, 15 %, 20 % and 40 %). It can be clearly observed that PAni with increasing contents of C<sub>60</sub> from 5 % to 10 % displays the ascending order of  $\varepsilon_r'$  from 5.98 to 9.97. However, the increasing contents of C<sub>60</sub> from 15 % to 40 %, the  $\varepsilon_r'$  shows the descending order from 7.84 to 4.35. Among all the PAni, PAni with 10 % of C<sub>60</sub> shows the highest  $\varepsilon_r'$  of 9.97.



**Figure 4.26:** Dielectric permittivity ( $\varepsilon_r'$ ) of PAni nanocomposites with different contents of C<sub>60</sub>: (a) 5 %, (b) 10 %, (c) 15 %, (d) 20 % and (e) 40 %

Theoretically, the electronic, ionic, orientation and space polarization are the main factors that contribute to the  $\varepsilon_{r'}$  (Zhao et al., 2014). Based on FESEM images as shown in Figure 4.22, PAni with 10 % of C<sub>60</sub> possesses the largest amount of nanorods/nanotubes with the biggest D that significantly enhance the heterogeneity of the nanocomposites. Therefore, it will ultimately induce the space charge polarization along the PAni backbone that significantly enhances the  $\varepsilon_{r'}$ .

Based on the result obtained, PAni with 40 % of C<sub>60</sub> revealed the lowest conductivity, heterogeneity (the lowest amount of nanorods/nanotubes with smallest D) and  $\varepsilon_{r'}$  (4.35) might lead to the lowest microwave absorption with the poorest EMI shielding properties. This phenomenon happen because the highest content of C<sub>60</sub> will induce the formation of more individual C<sub>60</sub> particles than the C<sub>60</sub> encapsulated PAni, thus decrease the molecular polarization along the PAni segments. Therefore, it eventually diminishes the current when incident EM waves penetrate the surface of PAni, hence reduce the microwave absorption (-6.3 dB).

Among all PAni, PAni with 10 % of C<sub>60</sub> possesses the highest  $\varepsilon_{r'}$  (9.97), heterogeneity (the largest amount of nanorods/nanotubes with the biggest D) and electrical conductivities (1.708 × 10<sup>-1</sup> S/cm) might improve the interchain and intrachain charge transfer as well as molecular polarization along the PAni backbone. Hence, it eventually reduce the electrical energy dissipated by PAni, finally enhances the EMI shielding efficiency with improved microwave absorption of -61.3 dB.

The main driving forces that play significant function in the enhancement of microwave absorption are the highest  $\varepsilon_{r'}$ , heterogeneity and electrical conductivities. Based on the result obtained, it is clearly observed that the addition of C<sub>60</sub> into PAni nanocomposites just plays a minor role in the enhancement of microwave absorption as well as EMI shielding efficiency of PAni. This proposed phenomena are the new discovery that found in this research study.

# CHAPTER 5: CONCLUSIONS AND SUGGESTION FOR FURTHER RESEARCH

## 5.1 Conclusions

In this study, several types of PAni nanocomposites with addition of dielectric material (TiO<sub>2</sub>) and different types of fullerene (C<sub>60</sub> and S.G.F) were successfully synthesized through template-free method. The addition of TiO<sub>2</sub> and fullerene do not affect the chemical structure of PAni nanocomposites since it showed similar pattern for all FTIR, UV-Vis and XRD spectra. Fullerene doped PAni nanocomposites with chemical treatment by CSA shows a better dispersion during polymerization, which significantly induced the formation of larger amount of nanorods/nanotubes (high heterogeneity), thus eventually improve the EMI shielding efficiency (RL = -61.3 dB) as compared those without and with chemical treatment by others sulfonic groups (RL from -37.2 dB to -53.0 dB). Besides, PAni with addition of C<sub>60</sub> shows a better synergy effect and significantly enhance the EMI shielding performance (RL -61.3 dB) as compared to those with S.G.F (RL = -9.3 dB).

Among all PAni nanocomposites, PAni with 10 % contents of C<sub>60</sub> possess the highest electrical conductivity (1.708 x 10<sup>-1</sup> S/cm), dielectric permittivity (9.97) and heterogeneity (larger amount of nanorods/nanotubes) will induce the strong charge transfer between PAni and C<sub>60</sub>. Then, it will cause more disordered motion of charge carrier along the PAni backbone and finally improved the EMI shielding efficiency with the highest RL of -61.3 dB at 9 GHz. On the other hand, C<sub>60</sub> just act as a secondary material in order to improve the conductivity and EMI shielding properties of PAni. This proposed mechanism and phenomena is the new discovery that found in this study. The PAni/HA/TiO<sub>2</sub>/C<sub>60</sub> (10 %) with chemical treatment by CSA that successfully synthesized in this study possesess the highest EMI shielding efficiency (RL = -61.3

dB) at 9 GHz is potentially applied in radar application which is operating in the frequency range of (8 - 12 GHz)

# 5.2 Suggestion for further research

For further study, different types of dielectric materials such as strontium titanate (SrTiO<sub>3</sub>) and barium titanate (BrTiO<sub>3</sub>) and carbonaceous materials such as C<sub>70</sub> or C<sub>84</sub> can be added in order to enhance the dielectric and magnetic property of the PAni nanocomposites.

Besides, different synthesis parameter such as different polymerization temperature (-5 °C, -10 °C or -20 °C), different types of dopant (hydrochloric acid, dioctyl sulfosuccinate sodium salt) can be modified in order to achieve excellent EMI shielding properties microwave absorption properties which can be potentially applied in numerous applications such as mobiles phones, radar and medical equipment.

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## LIST OF PUBLICATIONS AND PAPERS PRESENTED

## Articles published in ISI-cited journals:

- 1. Mokhtar, N., Desmond, A. T. C., & Phang, S. W. (2017). Morphology, conductivity and microwave absorption behavior of PAni nanocomposites after chemical treatment. *Journal Polymers & Polymer Composite*, 25(7), 545-554.
- Koh, Y. N., Mokhtar, N., & Phang, S. W. (2017). Effect of carbon nanotubes' dimension on microwave absorption property of polyaniline nanocomposites. *Journal Polymers & Polymer Composite*, 25(7), 527-536.
- 3. Koh, Y. N., Mokhtar, N., & Phang, S. W. (2016). Effect of microwave absorption study on polyaniline nanocomposites with untreated and treated double wall carbon nanotubes. *Polymer Composites*, *39*(4), 1283-1291.

## **Paper presented:**

- Mokhtar, N., Desmond, A. T. C., & Phang, S. W. (2017). Effect of microwave absorption properties with different contents of fullerene. 25<sup>th</sup> Annual World Forum on Advanced Materials (POLYCHAR 2017), 9<sup>th</sup>-13<sup>th</sup> October 2017, Putra World Trade Centre (PWTC), Kuala Lumpur, Malaysia.
- Mokhtar, N., Desmond, A. T. C., & Phang, S. W. (2016). Microwave absorption properties of polyaniline nanocomposites with different types of fullerene. 10<sup>th</sup> International Materials Technology Conference & Exhibition, (IMTCE 2016), 16<sup>th</sup>-19<sup>th</sup> May 2016, Putra World Trade Centre (PWTC), Kuala Lumpur, Malaysia.
- Mokhtar, N., Desmond, A. T. C., & Phang, S. W. (2015). Effect of microwave absorption study on fullerene doped polyaniline nanocomposites after chemical treatment. The 4<sup>th</sup> Federation of Asian Polymer Societies International Polymer Congress (4FAPS-IPC 2015), 5<sup>th</sup>-8<sup>th</sup> October 2015, Putra World Trade Centre (PWTC), Kuala Lumpur, Malaysia.